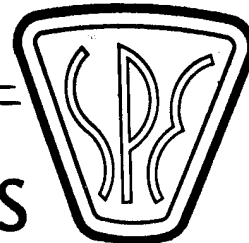


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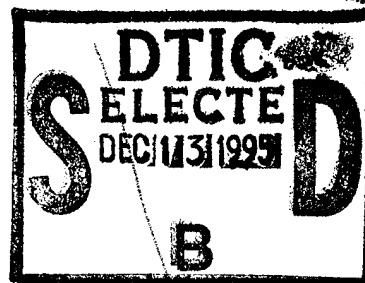
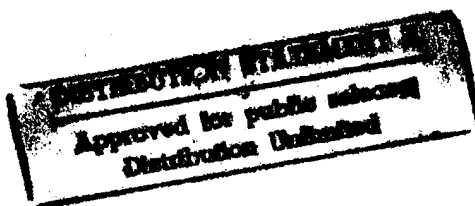
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8970-1

CORRELATION OF POLYMER STRUCTURE AND PROPERTIES

37

John R. Collier

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Athens, Ohio

The development of new polymers and a better understanding of existing ones has contributed greatly to the high sales figure for polymeric materials. During 1965 over 10 million pounds of polymers¹ were sold giving a total sales which exceeded that of all non-ferrous metals combined and was approximately one-fifth that of steel. The rate of increase has also been quite phenomenal with the sales figure for polymeric materials doubling approximately every six years.² This rapid growth can be maintained in the future by the development of additional new materials, but even more so by the development of a deeper insight into the effect of structure on polymer properties, and new processing techniques.

In the past and probably in the future, one of the greatest assets of polymeric materials has been and will be their intrinsic toughness. As a result of this toughness, these materials have been applied to many new uses. An example of this toughness is a drawn nylon filament which exhibits an ultimate tensile stress of 10.2 kg/mm².² This nylon sample is more than twice as strong as mild steel, and on a strength-to-weight basis would be more than twice as strong as the strongest steel commercially available. The basis of this toughness has been elucidated recently^{2,3} and as a result, the toughness of polymers should be more readily controlled in the future. However, this is not the only variable to be considered in materials selection. There are certain limitations which must be overcome before polymers can compete with metals and ceramics for many applications. Two of these undesirable properties are the time dependence of the Young's Modulus⁴ and environmental stress cracking.²

A great deal of the future of polymers also lies in the development of higher temperature stability, higher degrees of crystallinity, better control of physical properties of a given polymer, and broader utilization of composite materials. Classically higher temperature stability has been achieved by using silicone polymers. However, recent developments in carbon based polymers has lead to materials stable to approximately 1000°C, such as the type molecules produced by partial decomposition of polyacrylonitrile.⁵

In order to compete in new markets it has also been desirable to increase the Young's Modulus of polymers. In the past this has been achieved by orienting the polymer molecules in a preferred direction or directions. This technique does produce increased strength in the orientation direction or directions but also produces decreased strength in other directions. Another technique of increasing the modulus is increasing the crystallinity of the sample.⁶ Because semi-crystalline polymers are between 0 and 95% crystalline, most of them being approximately 50%, there is a definite future to this approach.

In order to increase the crystallinity of a given polymeric material, research has been conducted on the effect of varying the process conditions during crystallization of the polymerized material. This research has been quite fruitful, but additional work has indicated that the degree of crystallinity can also be drastically affected by the conditions existing during the polymerization process. An example of this is the use of stereospecific catalysts allowing the production of polymers which are crystallizable due to their regularity along the chain axis. Isotactic polypropylene, which is being used to a great extent today is a semi-crystalline polymer as a result of stereospecific polymerization. Whereas atactic polypropylene, the only form available before Natta and his coworkers developed the stereospecific catalysts, can not crystallize at all. Another less familiar example is polystyrene, which is commercially available as a glassy amorphous polymer in the atactic form. This form is normally polymerized without the use of a catalyst and cannot be used as a rigid polymer at temperatures in excess of its glass transition, 100°C . However, using a stereospecific catalyst isotactic polystyrene can be polymerized which due to its ability to crystallize, is no longer restricted by its glass transition but by its crystalline melting point, 230°C .

Since most commercially available stereospecific polymers do contain fractions of other specificity, their crystallinity falls short of that theoretically possible. By increasing the perfection of stereospecificity the degree of crystallinity and hence the modulus could be increased.

Another polymerization technique which yields quite high crystallinities but is not yet used commercially is solid state polymerization.⁷ In this technique, the monomer is crystallized into the desired shape and then polymerized by irradiation. If little rearrangement is necessary during polymerization, the resultant polymer has a very high degree of crystallinity, and therefore improved physical properties.

The use of composite materials comprises another area of major growth in polymeric materials. Combination of polymers' useful properties with the desirable properties of other materials can be achieved by making composites composed of both types of materials. This, of course, is not a new innovation even in the polymers field but does exhibit a great deal of promise for future expansion. Currently, composites of polymers and fiber glass are being used in this capacity. The fiber glass contributes high strength and the polymeric materials give toughness to the composite which counteracts the intrinsic brittleness of ceramics.

The final area to be covered in this paper, but by no means the only remaining area, is a better understanding of the effect of crystalline structure on polymer properties. At the present time an explosion of knowledge pertaining to the structure of polymers is taking place. This is illustrated by the conception of polymers as only ring compounds prior to Staudinger's work in 1920, to the revelation of the folded chain conformation of long polymer chains beginning in 1957 with the work of Keller, Till and Fischer. This work is being carried on quite ably by a number of investigators, and they are showing that in many systems polymer crystallization is not at all as Flory⁸ envisioned with his fringed micelle concept. Even though much work has been and is continuing to be done on the morphology of polymers, not much of this vast store of knowledge has been applied to the problem of the observable macro properties of polymers. This, therefore, is another area which should contribute quite heavily to the future growth of polymeric materials.

A few investigators have begun to apply this knowledge of polymer structure to varying the properties of polymers. Kargin⁹ has shown by varying the process conditions for both gutta percha and isotactic polypropylene that he could

control the tensile strength and ductility of these materials. The results of his tests on isotactic polypropylene are reproduced in Table I.

Unfortunately, the melt times and temperatures used were neither long enough nor high enough to allow temperature equilibration or even complete melting. The optical melting point of polypropylene is approximately 176°C and the equilibrium melting point is approximately 182°C . Therefore, even if these samples could have equilibrated they would not have been above their equilibrium melting point. Under these conditions only partial melting as described by Banks, Gordon and Sharples¹⁰ should occur at least at the short heating times and low temperatures. This was borne out by the appearance of many very small spherulites in Samples A and D with progressively larger spherulites occurring in Samples B and C. These small spherulites were evidently nucleated on crystalline remnants which were larger than the critical nucleus size. Keeping these qualifying conditions in mind, it is still possible to arrive at qualitative conclusions as a result of this work.

As the average spherulite diameter increased from approximately 10 microns in Sample A to 100 microns in B, and finally to approximately 400 microns in Sample C, the tensile strength decreased from 300 to 225 and then to 125 kg/cm². Therefore, the strength of this polymer was quite dependent on the crystallite size. That is, as the average crystallite size decreases the tensile strength increases. Another interesting conclusion which can be drawn from these results, is that as the crystallite size decreases the ductility of the sample increases. This can be seen by comparing the per cent elongation of Samples B and C, 25%, to the 500% elongation of Sample A. A close similarity is noted to the behavior of metals in which the ductility increases as the grain size decreases.

Further interpretation of this data becomes difficult because of the lack of complete melting in many of the samples. However, it is interesting to note that when a melt treatment temperature of 170°C . below the optical melting point was used, many small spherulites were again observed. The tensile strength of this sample, D, is close to that of A, which exhibited the same morphological characteristics, but the ductility of D was much lower.

The effect of crystallographic form on the mechanical properties of polypropylene can also be detected from this data. Sample E was prepared by melt treating at 210°C for 5 seconds and then quenching to -70°C . This quenching procedure produces the low temperature hexagonal crystal structure of polypropylene.⁷ Many small spherulites were observed in this sample as were in Samples A and D, however, due to its different crystallographic form, its mechanical behavior was quite different. The ductility of Sample E was only slightly higher than A, but the tensile strength of E was much lower than A.

Although the work of Kargin is only a beginning into this vast field of the relationship between crystalline structure and mechanical properties, it does show the importance of this relationship. In order to extend this work, more careful control of the process conditions need to be made and a more complete understanding of the resultant morphology is necessary. Therefore, additional studies must be conducted on a more basic level before correlating further this knowledge to the mechanical properties. One example of such a study has been made using isotactic polypropylene. This study revealed the average spherulite size in isotactic polypropylene can be varied by controlling both the crystallization temperature and the melt treatment temperature. A more convenient method of reporting this variation in spherulite size is to note the primary nuclei density in a crystalline sample. As the nuclei density increases the average final spherulite size necessarily decreases since each spherulite is a result of one nuclei.

Table II¹¹ illustrates the effect of crystallization temperature on the nuclei density of polypropylene samples following a melt history of 230°C for one hour. As shown in this table, the crystallization temperature increase causes a decrease in the nuclei density.

A similar effect is noted in Table III when isotactic polypropylene samples are crystallized at 138°C but the previous melt history is varied.¹¹ As the melt treatment temperature is increased the nuclei density again decreases and the average spherulite size increases. If the work of Kargin is correct the tensile strength and ductility of isotactic polypropylene should be altered by varying the melt treatment and crystallization temperatures.

In some polymers it is possible to extend the variation of crystallite size more orders of magnitude than was shown for isotactic polypropylene. Using poly[3,3-bis(chloromethyl)oxacyclobutane], tradename Penton*, normal spherulitic growth is observed to result from slow cooling or isothermal crystallization from the melt, as shown in Figure 1.¹¹ Since Penton has a slow crystallization rate it is possible to quench this polymer to a glassy amorphous state prior to the onset of crystallization. Such a glassy sample can then be isothermally crystallized by heating it above its glass transition. The morphology resulting from this crystallization process is shown in Figure 2.¹² This figure shows that the resultant crystallites are not spherulitic but are small disconnected lamellae approximately 100 Angstroms thick and 1,000 to 2,000 Angstroms in lateral dimensions. Under these conditions the nuclei density is approximately a factor of 10¹⁰ greater than observed during isothermal crystallization from the melt. Nonisothermal crystallization in temperature ranges between those discussed give morphological forms which are between those depicted in Figures 1 and 2. Therefore, it should be possible to greatly vary the mechanical properties of a polymer such as Penton over a much greater extent than shown for polypropylene.

Earlier it was mentioned that there appears to be at least a general similarity between polymers and metals with respect to the relationship between crystallite size and mechanical properties. However, this similarity should not be carried too far. The crystallites in polymeric materials are not as simple as are the grains in metallic systems. This increased degree of complexity is a result of the long chain nature of polymeric substances and their mode of crystallization. Semicrystalline polymers have been shown to be intrinsically tough materials as a result of their ability to impede the propagation of cracks through their crystalline mass. Frank² has attributed this property to the "tie molecules" which exist between and connect the various crystalline segments. As a result of these "tie molecules" extended across the noncrystalline regions, stress cannot be concentrated at the tip of a crack as greatly as in a metallic or ceramic system.

Keith and Padden³ have been able to observe these "tie molecules" in polyethylene as shown in Figure 3. This electron micrograph is of a mixture of fractionated polyethylene and the linear hydrocarbon n-C₃₂H₆₆. As revealed in this figure groups of "tie molecules" actually exist as intercrystalline links extended between both different sections of the same spherulite and between spherulites. These intercrystalline links are 30 to 300 Angstroms thick and up to 15,000 Angstroms long. The number of these links is a strong function of both the concentration of crystallizable components and of the crystallization temperature. As the concentration increases or as the crystallization temperature decreases, the number of these links increases. The tensile strength should also change with these variables since semicrystalline polymer samples have been shown to fracture both between spherulites and radially between crystalline portions of a spherulite. Therefore, the tensile strength and ductility of polymers must be dependent on the crystallization temperature and crystallite size in a

*Registered trademark Hercules Powder Co.

more complex manner than they are in metallic systems.

SUMMARY

As has been shown, the magnitude and growth rate of polymer sales is quite high and should continue to be so partially as a result of new materials, deeper insight into the effect of structure on polymer properties, and new processing techniques. Although new materials will continue to be developed, this paper has dealt primarily with improving the properties of existing materials to make them better able to fulfill existing and new applications. This will be done by applying the vast store of knowledge of the morphological characteristics of semicrystalline polymers to the tailormaking of the desired physical properties of a given polymer within the broad framework dictated by the polymer's chemical structure. Increased crystallinity as a result of increased knowledge and control of the polymerization and crystallization process conditions coupled with better techniques of predicting and controlling the mechanical properties will greatly aid in this task. As a result, the future of the polymer industry should continue to remain bright.

REFERENCES

1. Modern Plastics 43, 86 (1966).
2. Frank, F. C., Proc. Roy. Soc. A 282, 9, (1964).
3. Keith, H. D., Padden, F. J., Jr., and Vadimsky, R. G., J. Polymer Sci. A-2 4, 267 (1966).
4. Baer, Eric, "Engineering Design of Plastics", Reinhold Publishing Co., London (1964).
5. Mark, H. F., J. Polymer Sci. C #9, 1, (1965).
6. Matsuoka, S., Polymer Eng. & Sc. 5, 142, (1965).
7. Geil, P. H., "Polymer Single Crystals", Interscience Publishers, New York, (1963).
8. Flory, P. J., "Principles of Polymer Chemistry", Cornell University Press, Ithaca, New York (1953).
9. Kargin, V. A., Sogolova, T. I. and Nadareishvili, L. I., Polymer Sci., U.S.S.R., 6, p. 1404 (1964).
10. Banks, W., Gordon, M. and Sharples, A., Polymer 4, p. 289 (1963).
11. Collier, John R., Ph.D. thesis, Case Institute of Technology (1965).
12. Collier, John R., and Baier, Eric, J. Appl. Polymer Sci., to be published.

TABLE I

<u>Sample</u>	<u>Melt Temperature, °C</u>	<u>Melt Heating Time, sec.</u>	<u>Cooling Conditions</u>	<u>Tensile Strength, kg/cm²</u>	<u>Final Elongation, %</u>
A	180	5	60 min. at 80°C	300	500
B	180	20	60 min. at 80°C	225	25
C	180	60	60 min. at 80°C	125	25
D	170	5	60 min. at 80°C	275	60
E	210	5	Quenched to -70°C	150	625

TABLE II

<u>Crystallization Temperature, °C</u>	<u>Nuclei Density, nuclei/micron² x 10⁶</u>
119.2	11
132.7	7.0
136.2	6.6
137.0	4.1
139.0	1.6

TABLE III

<u>Melt Treatment Temperature, °C</u>	<u>Nuclei Density, nuclei/micron² x 10⁶</u>
194.1	22
198.7	22
217.6	8.0
220.6	6.4
224.9	1.5
225.0	2.9
230.3	1.6



FIGURE 1: Electron micrograph of a Penton sample crystallized from the melt at 154°C.

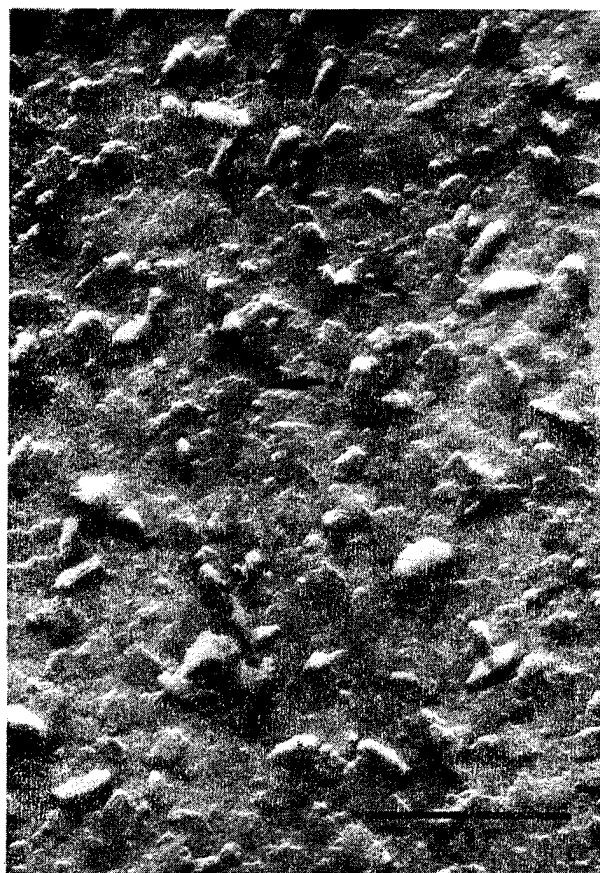


FIGURE 2: Electron micrograph of a Penton sample crystallized from the glass at 33.4°C.

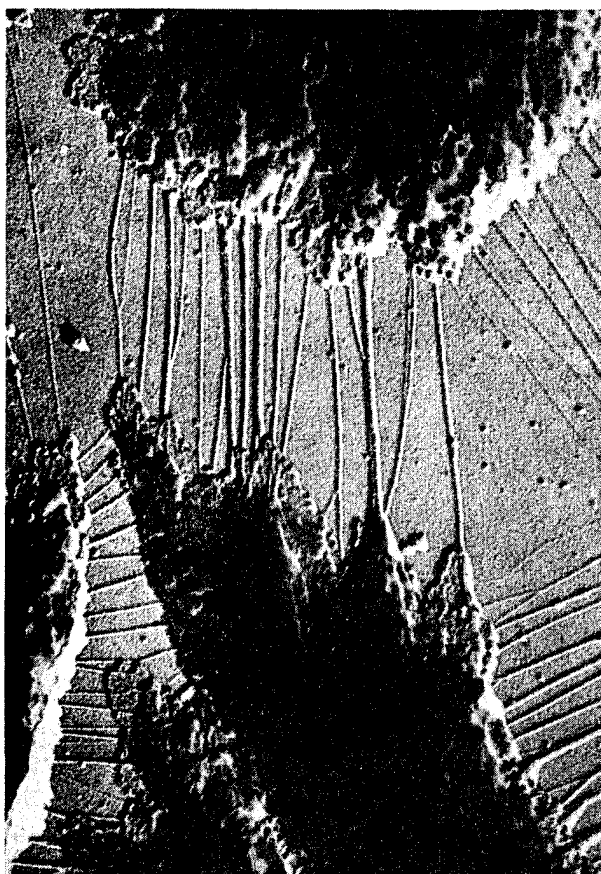


FIGURE 3: Electron micrograph of the intercrystalline links in a polyethylene sample crystallized at 110°C.

5970-2

CHLORINATED POLYETHYLENE

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and

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INTRODUCTION

Since prior to 1960, the Dow Chemical Company has been actively engaged in process and product research studies involving chlorinated polyethylene. (This paper discusses possible chlorine concentration variables as they affect various physical properties including density, relative crystallinity, permeability, 100% modulus, Shore 'A' hardness, elongation, ultimate tensile strength, and processability. Some extrapolation of data has been based upon the specific process and will not be completely valid for other methods of chlorination. Unless specifically stated otherwise, the products referred to are chlorinated linear homo-polymers. Also included are formulation requirements, potential applications, and fabrication techniques. Because of further expected advances in technology, even the wide range of possibilities shown does not adequately describe the versatility of this family of plastics.)

HISTORY

Chlorinated polyethylene was first introduced commercially in the 1940s. Because only low density polyethylene was available at the time, it was used as the base material for chlorination. Since this polyethylene was produced only in a granular form, it was necessary to dissolve it in an organic solvent (generally a chlorinated hydrocarbon) to carry out the chlorination. This product was rather expensive and had low tensile properties. It was used mainly as an additive to other plastics and did not reach large scale production volume.

Although present techniques permit low density polyethylene to be ground to extremely fine particle size, even the aqueous suspension chlorination techniques of today yield a product of rather low tensile properties.

With the discovery of high density polyethylene in the middle 1950s, new base polymers became available for chlorination. These resins, when chlorinated, showed physical properties far superior to those of previously available polyolefins. Because the Ziegler slurry process produced high density polyethylene in a finely divided powder form, this material could be readily chlorinated in simple aqueous suspension as well as in solution. This allowed additional process parameters, through which physical properties could be controlled and the products tailored to fit specific needs.

PROCESS VARIABLES

In developing the family of chlorinated polyethylenes to be described here, a number of raw materials and process variables have been studied.

CHLORINATED POLYETHYLENE

The process is essentially a chlorination of high density polyethylene homo-polymers and copolymers in water slurry. The basic parameters include parent resin, chlorine content, and mode of chlorination. Chlorine contents studied have ranged from below 10 to above 70%, with the major concentration on 25 to 50% chlorine, the region of greatest product flexibility. Parent polyethylenes studied ranged from molecular weights of less than 20,000 to greater than 4 million, with the area of concentration being from 20,000 to about 300,000.

A. Discussion

The process parameters involved allow the production of chlorinated polyethylenes with a wide range of physical properties. To correlate these properties, the attainable range for a specific property will be shown as a function of chlorine content. The relationships among the various properties will then be covered and specific properties of some standard development materials briefly summarized. Potential applications as related to these physical properties will also be pointed out.

B. Density

As could be anticipated, product density is the property which is least influenced by the method of chlorination. Figure 1 shows the variation of this property from approximately 10% chlorine up to about 57% chlorine. Regardless of the mode of chlorination, the density of a particular product will fall within about 0.02 g/cm³ of this line.

Polyethylenes chlorinated to achieve maximum destruction of crystallinity (i.e., to achieve maximum flexibility) at low chlorine contents will have slightly higher densities.

C. Crystallinity

A quantity which we use as a one measure of the randomness of chlorination is the per cent relative crystallinity of the chlorinated polyethylene, as determined by X-ray diffraction. To distinguish this from the absolute crystallinity, we define it simply as the ratio of the area under the crystalline peaks to the total area of the X-ray Diffractometer scan from $2\theta = 14^\circ$ to $2\theta = 28^\circ$, i.e.,

$$\% \text{ Cryst. Rel.} = \frac{C_1 + C_2}{C_1 + C_2 + A} \times 100$$

(Figure 2). The equation* developed by Aggarwal and Tilley for calculation of the crystallinity of polyethylene is not applicable

*Aggarwal, S. L., and Tilley, G. P., J. Pol. Sci., XVIII, pp. 17-26 (1955).

because of the change in the diffraction characteristics of the chlorinated amorphous regions of the polymer. So, although we refer to the relative crystallinity of our parent polyethylenes as being 40 to 50%, we are referring to linear materials.

The variation of this relative crystallinity with chlorine content is shown in Figure 3.

Also on this curve are points corresponding to four developmental materials. The same four materials will also appear on later graphs. Values on this and later plots refer to properties obtained on materials which have been stabilized, milled and compression molded.

At a given chlorine content, the chlorinated polyethylene having lower relative crystallinity will generally be the more flexible.

D. Permeability

The permeability of chlorinated polyethylene can be varied over a very wide range, depending on the chlorine content and mode of chlorination. Figure 4 shows a plot of nitrogen permeability at 23°C versus chlorine content.

The upper curve shows values obtained for relatively amorphous materials, while the lower curve is one extrapolated from limited data for materials of relatively high crystallinity. The values here, and in the following permeability plots, should only be interpreted relatively because they are taken from data obtained on films as thick as 15 mils and are normalized to unit thickness.

Figure 5 shows water vapor transmission vs. chlorine content.

It is worth noting here that at the higher chlorine contents it is possible to obtain chlorinated polyethylenes showing less water vapor transmission than does poly(vinyl chloride), (PVC).

Figure 6 shows oxygen permeability as a function of the chlorine content at various temperatures. Again, these curves are for relatively amorphous materials and they could readily be shifted downward by chlorinating in a manner to retain crystallinity.

E. 100% Modulus

A test commonly employed as a measure of flexibility of plastics is the 100% modulus, i.e., the stress required to elongate the specimen 100%. Figure 7 shows the range which is attainable in chlorinated polyethylene. The lower the value of the 100% modulus, the greater the flexibility of the material. There is a strong tendency for the amorphous CPEs to have lower modulus values but this also is influenced by the mode of chlorination. Particularly in the range of 30 to 45% chlorine this relationship with crystallinity does not always hold true.

F. Hardness

Another property indicative of the flexibility of chlorinated polyethylene is Shore^{°A} Hardness. There is a good correlation between

100% modulus and hardness, as shown in Figure 8.

A given value of 100% modulus corresponds to a hardness range of about 10 points. This is attributable to the "creep" or cold flow characteristics of chlorinated polyethylene. The hardness is measured according to ASTM D-1706 with a reading taken after 15 seconds. So, if two samples having identical modulus values are compared, that sample having the greatest tendency to cold flow will have a lower hardness value. Two factors which significantly affect hardness are relative crystallinity and molecular weight of the parent polyethylene. An increase in either of these factors tends to decrease cold flow characteristics and thereby increase measured hardness.

G. Elongation

Figure 9 shows elongation break vs. chlorine content. Chlorinated polyethylenes having high elongations are available over an extremely wide range of chlorine contents. Not all of the elongation, however, can be characterized as "usable". A look at the stress-strain curves shown in Figure 10 will illustrate this. Chlorinated polyethylenes having either very high or very low chlorine contents tend to exhibit curves of the type numbered "1", i.e., the stress rapidly approaches a maximum yield value with the sample breaking thereafter at some lower stress. More flexible or elastomeric chlorinated polyethylenes exhibit curves of type Number "2", wherein there is a slight yield near 100% elongation with the stress increasing thereafter to a maximum value at which the sample breaks. Virtually all types of curves falling between these two extremes are obtainable.

H. Ultimate Tensile Strength

Figure 11 shows ultimate tensile strength vs. chlorine content. Maximum values shown at the extremes of chlorine content are tensile yield values rather than tensile at break, because we consider the former to have greater meaning.

One characteristic of the essentially amorphous chlorinated polyethylenes, except at very high chlorine contents, is a decrease in tensile strength with increasing temperature. Figure 12 shows a physical property profile from -50 to 180°F of a sample containing 35-40% chlorine and having essentially no crystallinity.

As can be seen from this plot the range of maximum utility for a highly flexible, thermoplastic chlorinated polyethylene is at relatively low temperatures. At higher temperatures, however, it can be used in applications as a flexible membrane where it is subjected to little or no stress, or is reinforced. The properties in the preceding Figure 12, incidentally, were obtained using a non-ASTM sample. The environmental cabinet used in determining the properties allowed only about 7" of pull and it was, therefore, necessary to use a specimen having a much shorter restricted section. The rate of strain was, however, essentially that prescribed by ASTM.

The range of properties shown in these preceding plots is not meant

to imply that one has merely to point out a desired property value from each curve and polyethylene can be chlorinated in such a fashion so as to give the total combination of properties. If, for example, a very flexible material is desired, one must be willing to accept an intermediate tensile strength (ca. 1500 psi) and a relatively high elongation (400% or greater). Low 100% modulus, low tensile strength, and high elongation tend to accompany one another. Control of these relationships is primarily through control of the chlorine content and the parent polyethylene.

I. General Characteristics

Figure 13 gives some idea of the general physical characteristics attainable with chlorinated polyethylene over a wide range of chlorine contents.

The lowest range shown on this diagram exhibits properties very similar to those of the ethylene-vinyl acetate copolymers. The elastomeric range, which is by far the widest, generally shows properties similar to those of flexible vinyl and rubbers. The mid-point of this range shows the most rubber-like characteristics.

Designation of one range as "semi-rigid" is rather an arbitrary characterization, because chlorinated polyethylene can be made essentially semi-rigid at any chlorine content.

Rigid chlorinated polyethylenes have physical properties similar to those of PVC at ambient temperatures. The glass transition temperature at about 57% chlorine content can, however, be significantly lower than that of PVC.

At the extreme upper end of the diagram the properties of chlorinated polyethylene become very much like those of chlorinated PVC. Both tensile strength and heat distortion temperature become higher than those of PVC and the material becomes more difficult to process.

J. Processability

Linear chlorinated polyethylenes show generally good processability. Figure 14 is a plot of Apparent Shear Stress vs. Apparent Shear Rate for several materials. The linear polyethylene included in this plot for comparison is a 0.8 M.I. homopolymer. PVC 111-4 is classified as a medium molecular weight polyvinyl chloride.

While the melt viscosity of chlorinated polyethylene is significantly higher than that of plasticized PVC 111-4, it is also significantly lower than that of unplasticized PVC 111-4. Because of high shear sensitivity, chlorinated polyethylene is more readily processed than its melt index value at low shear rates would indicate. Substituting a parent polyethylene of lower molecular weight gives chlorinated polyethylene of even lower melt viscosity.

Amorphous chlorinated polyethylenes of intermediate chlorine content can be banded on a cold mill. They can be effectively blended with additives on a roll mill at temperatures of 200° to 400°F, and

have also been extruded within this temperature range. A Mooney viscosity of 40-50 at 250°F is typical for the raw resin.

K. Development Materials

Table I describes some of the resins which have reached development stage. This table is by no means complete and is intended only to give some idea of the types of materials which will soon be available commercially.

L. Formulation Requirements

Properties given in Table I are for stabilized formulations, but the resin as produced contains no stabilizers and is in the form of small, white granules or "crumbs" which are well suited for dry blending. As with other chlorine-containing polymers, it is necessary to formulate the chlorinated polyethylene with additives to withstand processing and service conditions. CPE responds extremely well to conventional PVC stabilizers and polyolefin antioxidants.

Elastomeric chlorinated polyethylene can be loaded to high levels and still retain flexibility. Some formulations containing over 50% by weight of fillers have not shown excessive loss in physical properties.

POTENTIAL APPLICATIONS

A. Polymer Modifier

In general, chlorinated polyethylene of intermediate chlorine content (25-45%) shows excellent compatibility with both polyethylene and PVC. At low concentrations in PVC excellent impact improvement is attained, and at higher levels the chlorinated polyethylene serves as a permanent plasticizer. Chlorinated polyethylene shows significant advantages over plasticized PVC, particularly in applications where it will be subjected to outdoor weathering. Its inherent flexibility will be lost only if it has undergone significant decomposition. Since no plasticizers are necessary, problems associated with plasticizer loss are eliminated. Low temperature flexibility is also much better.

Chlorinated polyethylene can be blended with other polyethylenes to make a flame retardant material of increased flexibility and improved stress-crack resistance.

B. CPE Compounds

Chlorinated polyethylene itself has good flame retardant characteristics. Above 40% chlorine, it becomes completely self-extinguishing.

Since this material is completely saturated, it shows excellent ozone resistance. Heat stability, when properly formulated, is very good. Weatherability of chlorinated polyethylene is also excellent. Some formulations on weathering racks for about three

years still have over 90% of their original tensile strength and elongation, as measured on samples of approximately 60-80 mils thickness.

Solvent resistance is very similar to that of PVC. Resistance to most salts, bases and acids is quite good, so chlorinated polyethylene shows promise as a liner for storage tanks for these materials. CPE shows poor resistance to aromatics and ketones. In at least one respect this may be an advantage because the amorphous chlorinated polyethylenes at chlorine contents of 35% and higher can be solvent welded with xylene, toluene, methyl ethyl ketone and tetrahydrofuran.

One interesting application is the use of chlorinated polyethylenes in film. Variation in permeability characteristics by different levels and modes of chlorination allows "tailoring" to an end use. Polyethylenes chlorinated to levels of 50% or more can be cast from solvents because of the exceptional solubilities in such common organic solvents as toluene, methyl ethyl ketone and tetrahydrofuran. Ten percent or more by weight can be dissolved using high shear mixing without external heat.

In addition to organic solvent solubility, chlorinated polyethylenes generally have better adhesion to metals and other materials than PVC. They also show good adhesion when laminated to many other plastics.

A very broad field of potential applications is in wire and cable coatings and gasketing. Chlorinated polyethylenes can be made thermosetting by cross-linking, and the resulting materials show great improvement in high temperature properties, cold flow characteristics, tensile strength, and resistance to organic solvents. Further, ozone resistance is maintained and heat resistance can be truly exceptional. It would not be unreasonable to project continuous service temperatures of 100°C or higher.

It would not be practical to attempt to cover all, or even a significant portion of specific potential applications of chlorinated polyethylenes. To date, CPEs have been extruded, calendered, solution cast, blow molded and injection molded into many shapes and profiles, and yet this has been only a beginning. Evaluation of potential applications will uncover other uses for this family of plastics materials. Future papers will cover these applications in detail.

TABLE I

PROPERTIES OF CHLORINATED POLYETHYLENE

<u>QX 2243</u>	<u>.4</u>	<u>.6</u>	<u>.7</u>	<u>.8</u>	<u>.9</u>	<u>.10</u>	<u>.13</u>	<u>Test Methods</u>
Bulk density, lbs cu.ft.	25	32	11	17	20	12	16	Dow Test
Melt flow, 150 sec l, psi ± 5	31	32	27	46	32	33	52	Dow Test
Chlorine content, % ± 1	36	42	25	36	36	42	36	Dow Test
Relative crystall., %	0-10	< 2	15-20	0-5	< 15	5-10	0-5	Dow Test
Tensile strength, psi ± 200	1650	1300	1600	1500	1800	1800	1500	ASTM D412-62T*
Ultimate elong., % ± 100	850	600	700	700	700	600	700	ASTM D412-62T*
100% Modulus, psi ± 25	180	200	500	200	300	250	200	ASTM D412-62T*
Hardness, Shore "A" ± 5	50	47	75	50	62	56	50	ASTM D1706 (15 sec)
Low temp., brittleness, °F			— 50 to — 80					ASTM D746
Tension set, %	12	23	33	11	12	8	9	ASTM D412

*Type C Dumbbell

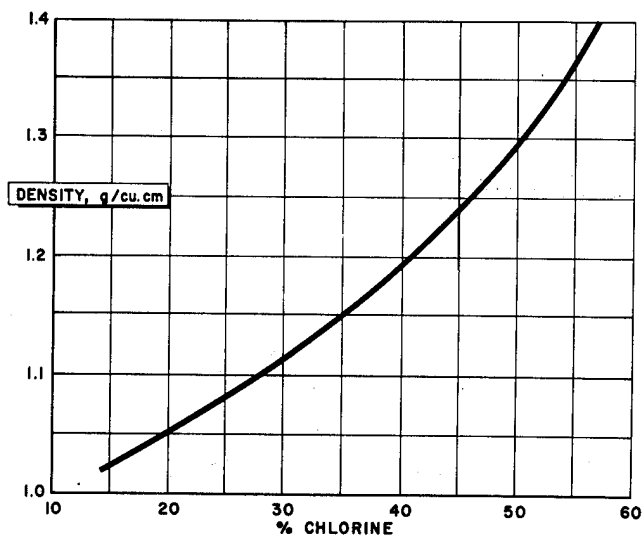


FIGURE 1

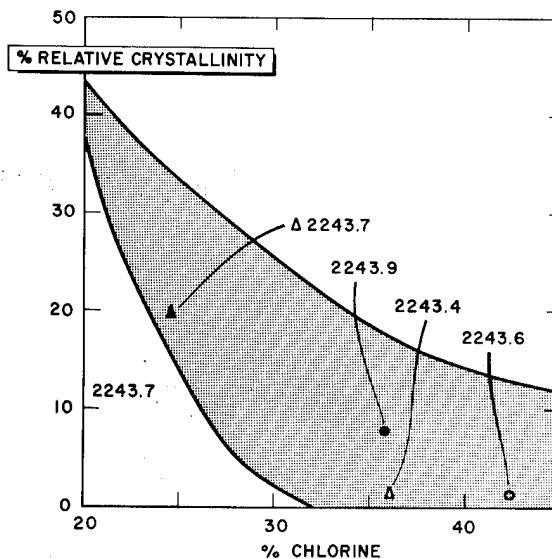


FIGURE 3

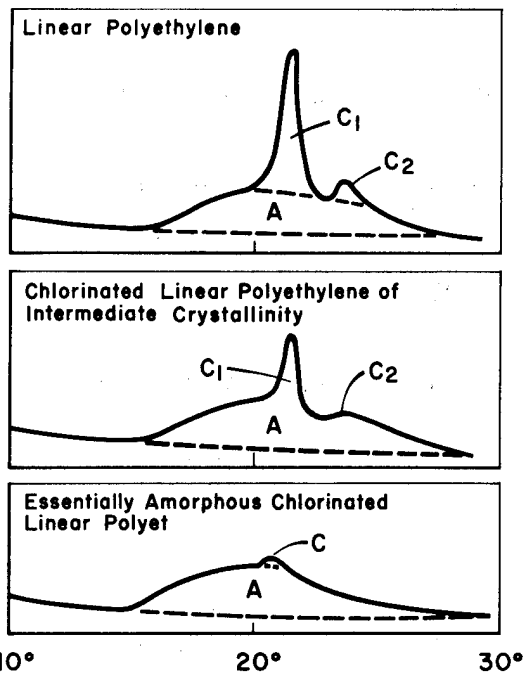


FIGURE 2

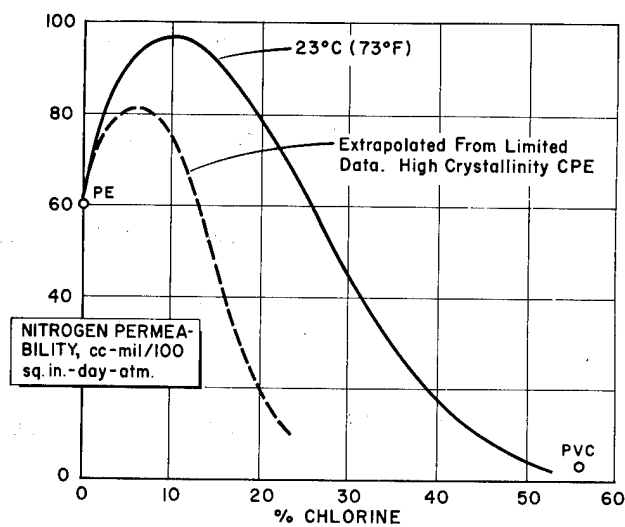


FIGURE 4

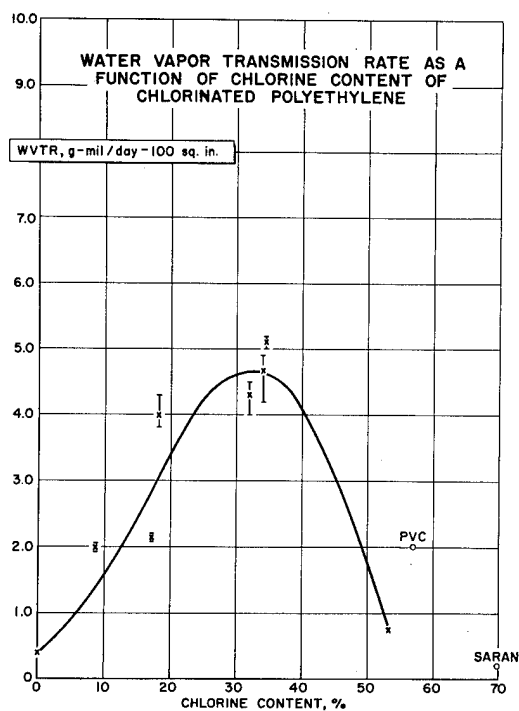


FIGURE 5

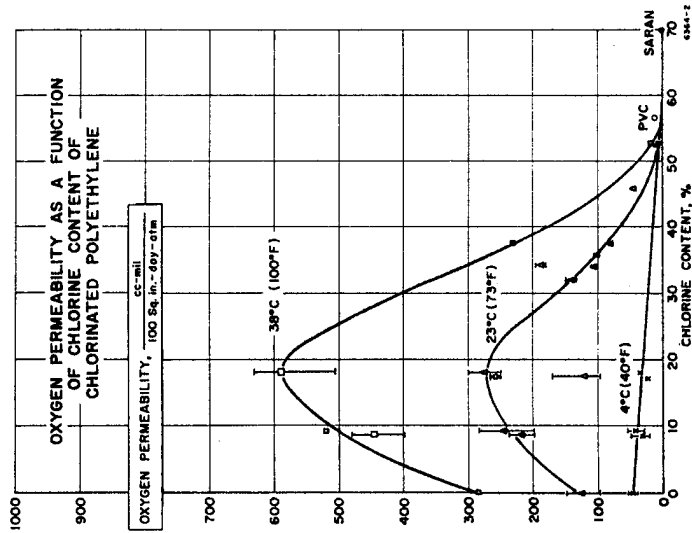


FIGURE 6

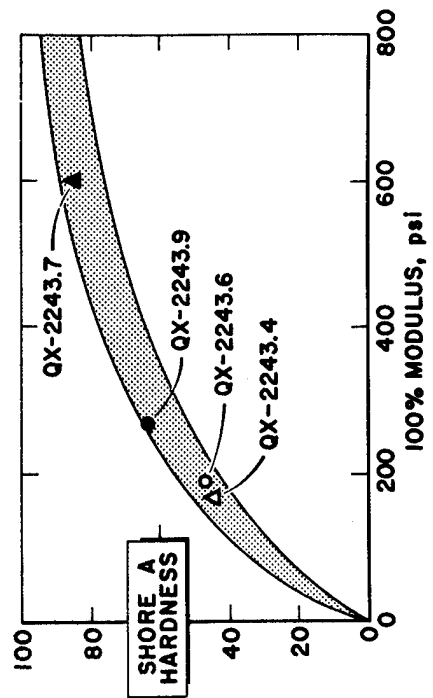


FIGURE 8

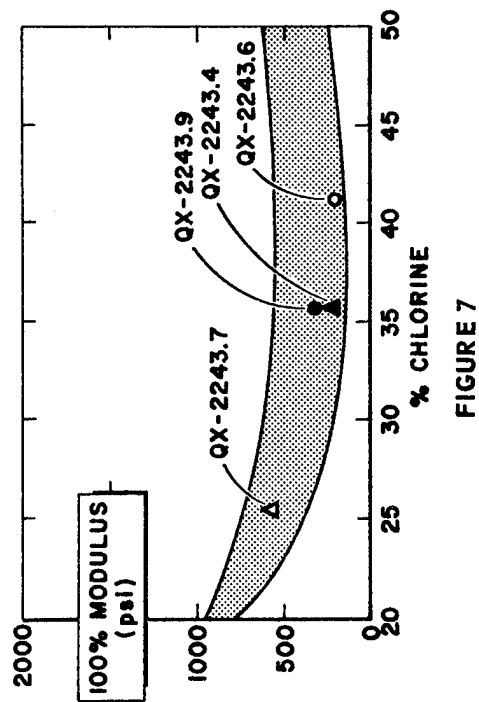


FIGURE 7

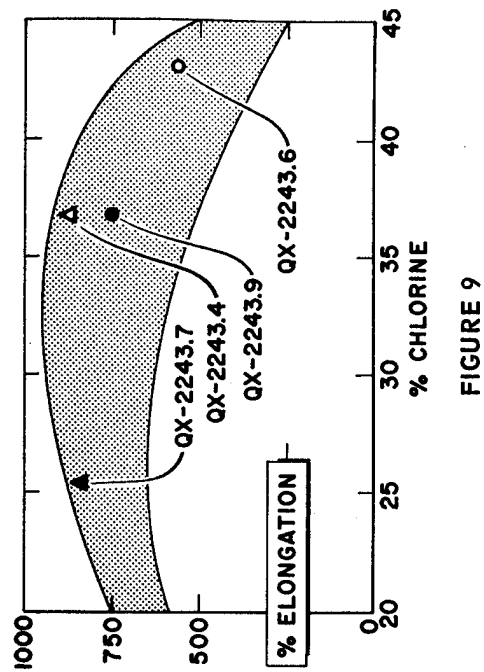


FIGURE 9

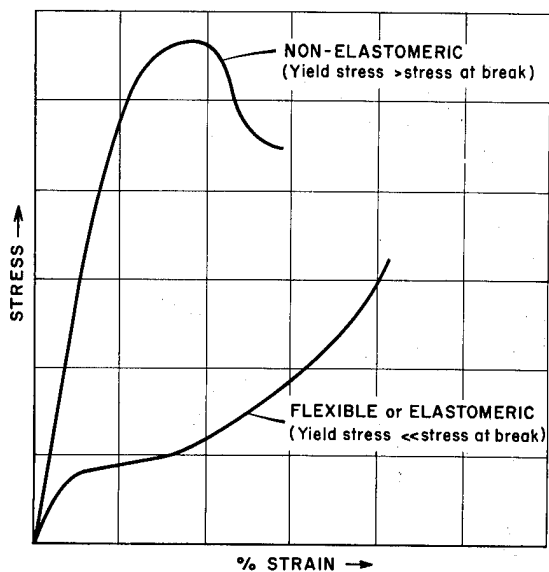


FIGURE 10

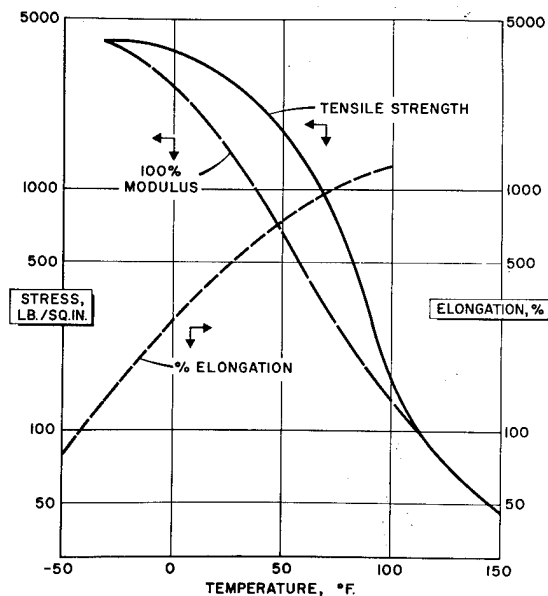


FIGURE 12

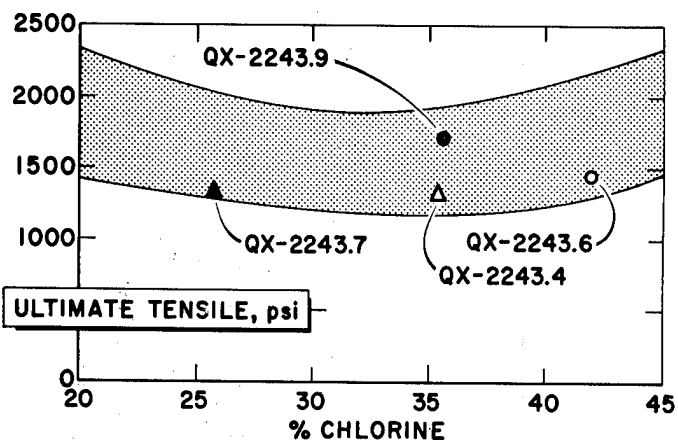


FIGURE 11

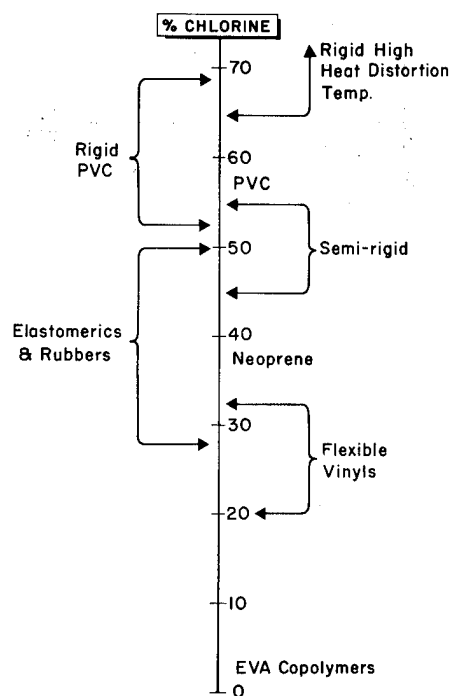


FIGURE 13

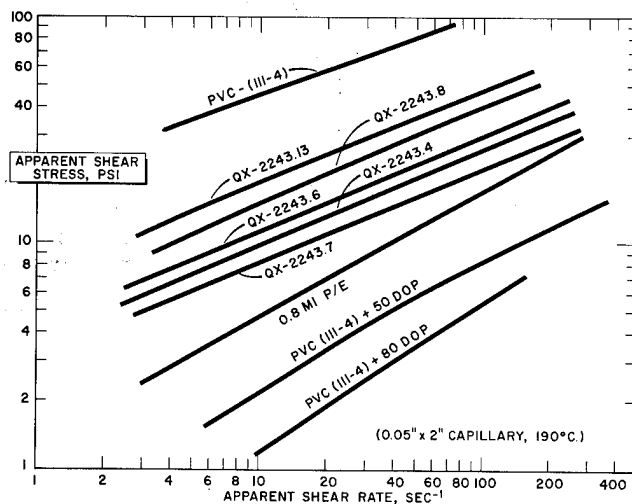


FIGURE 14

POLYARYLOXYSILANES

W. R. Dunnavant, R. A. Markle and P. B. Stickney

Battelle Memorial Institute

Columbus, Ohio

and

J. E. Curry and J. D. Byrd

National Aeronautics and Space Administration

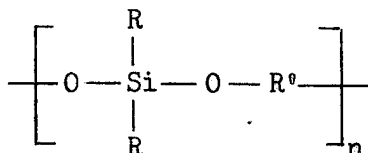
Huntsville, Alabama

INTRODUCTION

The successful use of silicones in high temperature applications for almost a quarter of a century has prompted extensive research efforts to provide improved polymers through modifications of the polysiloxane chain.

Examples of the approaches followed include the total or partial replacement of the silicon atoms by various elements from Groups III to VI of the Periodic Table;^{1,2} of the oxygen atoms by nitrogen, as in the polysilazanes;³⁻⁶ and the inclusion of silicon-carbon linkages within the polymer chain, as in the polysilphenylenes.^{7,8}

The present paper is concerned with a class of polymers, the poly(aryloxysilanes), which contain silicon-oxygen-carbon linkages in their main chains, and have the general formula



where R^0 is an aromatic unit, and R may be either an aromatic or aliphatic radical.

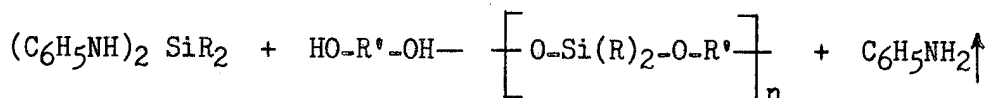
The poly(aryloxysilanes) possess high thermal stabilities as a result of the aromatic units and silicon-oxygen and phenoxysilane linkages in their chains, and the attachment of aromatic or aliphatic (preferably methyl) pendent groups to the chains through silicon-carbon linkages. In addition, the silicon-oxygen chain linkages provide highly mobile polymer chains but, as a result of the rigid aromatic chain units, less mobility than found in polysiloxane chains. The thermoplastic

polyaryloxysilanes are processable on standard equipment, and have potentially useful engineering properties.

Poly(aryloxysilanes) have been prepared by the alcoholysis of dialkoxy-silanes by aromatic diols,⁹ and the condensation of dihalosilanes with aromatic diols.^{9,10} Polymers containing both aryloxysilane and silazane linkages in the main chain have been prepared by the condensation of cyclosilazanes with diols.¹¹ However, these procedures appear to have led only to relatively low molecular weight silicon-containing polymers.

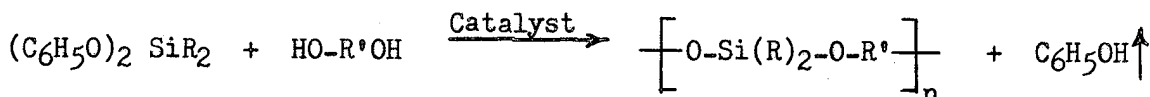
DISCUSSION

Two promising synthetic routes to relatively high molecular weight poly(aryloxysilanes) have been investigated recently. These depend upon the nucleophilic displacement of aniline from a dianilinosilane by an aromatic diol,¹²



Scheme I

or displacement of phenol from a diphenoxysilane by an aromatic diol in the presence of a catalyst.¹³



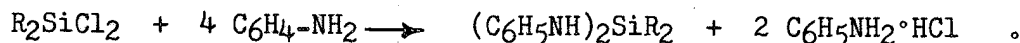
Scheme II

The polymers obtained by the two procedures are similar in nature, and exhibit generally high thermal stabilities. The poly(aryloxysilanes) have been prepared as soluble, film- and fiber-forming thermoplastics having up to 200 silicon atoms per molecule; as materials that are gum-like at room or elevated temperatures; and as insoluble products that are nonfusible at 350°C. Polymers prepared by Scheme I are stressed in the present work, and the polymer in which R is phenyl and R' is p,p'-biphenyl, is discussed as a model system.

EXPERIMENTAL

A. Monomers

The methyl- and phenyl-substituted dianilino- and diphenoxysilane monomers I-IV (Table I) were prepared and condensed with a variety of aromatic diols. The dianilinosilane monomers I-II were prepared by a modification of the procedures of Anderson,¹⁴ Curry and Byrd,¹² and Larsson and Smith,¹⁵ which involve the condensation of a dichlorosilane with excess aniline

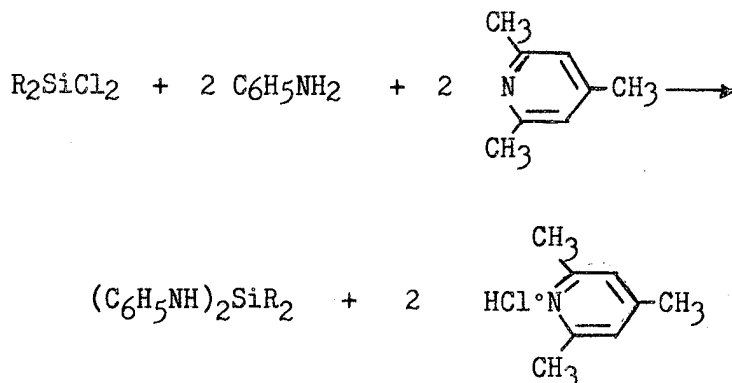


Anderson¹⁴ and Benkeser¹⁶ have shown that the conversion of a chlorosilane to an aminosilane is a reversible reaction. In the preparation of Monomers I and II, the resulting equilibria produce appreciable

quantities of the corresponding monoanilinosilanes



which reduce the yields of the desired monomers and complicate their isolation as pure materials. Improved yields (up to 80 per cent) of high purity Monomers I-II were obtained by condensing two moles of aniline with one mole of dichlorosilane in the presence of excess 2,4,6-trimethylpyridine (s-collidine). The collidine, which does not itself react with the chlorosilanes, is presumed to function as a preferential HCl acceptor because of its higher basicity than aniline, and to form a hindered salt incapable of reacting with the dianilinosilane monomers to generate the monoanilinochlorosilanes.



The diphenoxy Monomers III and IV were readily prepared by the condensation of the corresponding diphenyldichlorosilanes with phenol, and were isolated and purified by vacuum distillation.

B. Polymerizations

Monomers I-IV readily underwent melt polymerization with equimolar amounts of various aromatic diols. The intimately mixed silane and diol monomers were heated under nitrogen until homogeneous melts were obtained, and the polymerizations were then carried out at temperatures ranging from 200 to 300°C under a vacuum or nitrogen sweep. Upon fusion, Monomers I and II condensed very rapidly with the diols. Under similar polymerization conditions, Monomers III and IV condensed only slowly. The rates of the latter polymerizations were greatly enhanced by the inclusion of catalytic amounts of lithium, sodium, or potassium in the monomer mixtures.

C. Molecular Weights

The molecular weights reported in this paper were obtained by gel permeation chromatography (GPC) using a Water's Gel Permeation Chromatograph, and 1,2,4-trichlorobenzene as a solvent for the polymers. The molecular weights of randomly selected polymer samples were checked by light scattering. The GPC-determined molecular weights were found to be in excellent agreement with the values obtained by light scattering.

RESULTS

Typical poly(aryloxydiphenylsilanes) prepared from Monomers I and IV and aromatic diols using the above-described procedures are shown in Table II. The molecular weights indicated do not represent the maximum obtainable for the specific polymer structures shown. The polymers described in Table II were transparent, soluble thermoplastics. They varied from hard, brittle glasses to tough, flexible materials, depending upon their molecular weights. In each case, fibers could be drawn from the polymer melts. The polymers varied in color from light yellow to amber.

Crosslinked poly(aryloxysilanes) were obtained by prolonged heating or exposing the monomer mixtures to air at about 300°C during polymerizations. The degrees of crosslinking varied. For example, samples of polymers from Monomer I and p,p'-biphenol were prepared which were insoluble and nonfiber-forming, but which could be compression molded at moderate temperatures and pressures. More highly crosslinked forms of this polymer were obtained that were insoluble and did not soften or flow when attempts were made to compression mold them at 350°C under high pressures.

The poly(aryloxysilanes) appear to be amorphous materials which do not show true melting points. Differential thermal analyses of representative poly(aryloxysilanes) show no endotherms between 25 and 300°C indicative of either glass transition or crystalline melting temperatures. The polymer softening temperatures shown in Table II indicate the temperatures at which the polymers soften and begin to stick to a heated metal surface, and were determined using a Fisher-Johns Melting Point Apparatus. As might be expected, the larger, more rigid aromatic chain constituents provided polymers having higher polymer softening temperatures.

A series of representative poly(aryloxysilanes) prepared from p,p'-biphenol and Monomers I, II, III and IV are shown in Table III. These preparations illustrated that diphenyl-, phenylmethyl-, and dimethylsilyl-containing poly(aryloxysilanes) could be prepared with comparable ease by the same polymerization methods. As in the case of the poly(aryloxydiphenylsilane) polymers shown in Table II, the polymers containing phenylmethyl- and dimethylsilyl chain units were obtainable as tough, transparent, soluble solids which could be molded and drawn into fibers. The replacement of the pendent phenyl groups on the poly(aryloxysilane) chains by methyl groups was observed to generally improve the flexibilities of the polymers, but to reduce their polymer softening temperatures.

The condensations of Monomers I and II with aromatic diols were extremely rapid and high polymers were formed within a few minutes at polymerization temperatures of 200°C or higher. Condensations of Monomer I with p,p'-biphenol showed that relatively high molecular weight polymers could be obtained under a variety of polymerization conditions. It was observed that polymerizations could be carried out satisfactorily under a nitrogen sweep, vacuum, or under air at temperatures up to 250°C. However, exposure of the monomer mixtures to air at 300°C was found to lead to discolored and frequently highly crosslinked products.

A. Polymer Structures

The majority of the poly(aryloxysilanes) prepared were soluble in solvents, such as tetrahydrofuran, dimethylformamide, dimethylsulfoxide, and 1,2,4-trichlorobenzene, and are considered to be linear structures corresponding to the general formula. Typical elemental analyses (Table IV) and infrared analyses (Figure 1) are in general agreement with the formulae.

Typical infrared spectra of polyaryloxysilanes containing common biphenyl chain components, but differing silyl units are shown in Figure 1. The polymer (Spectrum A) containing the diphenylsilyl unit indicated several characteristic infrared bands. These included bands at 720 and 690 cm^{-1} arising from the monosubstituted aromatic rings attached to silicon, and a sharp band at 1429 cm^{-1} and broad band at 1125 cm^{-1} attributed to the Si-C $_6$ H $_5$ linkage. The 1,4-phenylene units in the chains showed absorption between 824 and 835 cm^{-1} due to C-H out-of-plane deformation. The Si-O linkages gave rise to a broad band system between 1200 and 1300 cm^{-1} which appeared in the spectrum of each polyaryloxysilane and is apparently characteristic of the phenoxysilicon linkage. The replacement of the diphenylsilyl unit by methylphenylsilyl (Spectrum B) was accompanied by the appearance of a C-H stretch absorption at about 2900 cm^{-1} , and a decrease in the phenyl absorption at 3030 cm^{-1} . This effect was intensified for those polymers (Spectrum C) containing dimethylsilyl chain units.

B. Thermal Stability

Typical thermogravimetric analyses of poly(aryloxysilanes) containing diphenylsilyl units are shown in Figure 2. These thermograms, obtained under nitrogen using a heating rate of 4 degrees per minute, indicate thermal breakdown temperatures in the 400-500°C range with appreciable polymer residues remaining up to 900°C.

The thermal-oxidative resistance of the poly(aryloxydiphenylsilanes) appears to be good. Thermal decompositions began at about 400°C under both nitrogen and air, although the decomposition under air was, of course, more catastrophic.

Thermograms of poly(aryloxysilanes) containing diphenyl-, phenyl-, methyl-, and dimethylsilyl chain units (Figure 3) indicated that polymers of each of these types exhibit high thermal stabilities. As might be expected, the fully aromatic-substituted poly(aryloxysilane) appeared to be the most stable.

PROCESSING AND PROPERTIES

Limited processability and property evaluation studies have been carried out on model polyaryloxysilanes prepared from dianilinodiphenylsilane and p,p'-biphenol. These polymers are typical thermoplastics and can be compression or injection molded, or extruded at 150-200 C/1000-2000 psi. The mechanical properties of these polymers having molecular weights (M_w) below about 45,000 were poor, but higher molecular weight materials showed significantly improved properties. Typical properties observed for the diphenylsilylbiphenyl polymers having molecular weights in the 49,000 to 84,000 range were:

Flexural strength, psi	3,000 - 10,000
Tensile strength, psi	3,000 - 8,000
Heat deflection temperature, °C (264 psi)	95 - 108
Impact strength, notched Izod, ft-lbs/inch of notch	0.18 - 0.43
Thermal breakdown temperature, °C (by TGA)	> 400
Per cent elongation	< 5

The same polymers could be cast from aromatic solvents to produce transparent films which could be creased sharply without cracking, and showed tensile strengths up to 6,000 psi. Chemical resistance and reaction tests indicated that the polyaryloxy-silanes are resistant to at least short-term exposures to water, and aqueous sulfuric acid or sodium hydroxide. They are soluble in a variety of aromatic solvents from which they can be readily converted into films or surface coatings.

CONCLUSIONS

[It has been established that a variety of poly(aryloxysilane) polymers can be conveniently prepared via the condensation of diphenoxy- and dianilinosilane monomers with aromatic diols. This study is being extended to include syntheses and evaluations of polymers containing several different silyl and/or aromatic chain units, and poly(aryloxysilanes) that are controllably crosslinkable.]

ACKNOWLEDGMENT

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REFERENCES

1. Lappert, M. F. and Leigh, G. L., "Developments in Inorganic Polymer Chemistry", Chapters 7 and 8, Elsevier Publishing Co. (1962).
2. Stone, F. G. A. and Graham, W. A. G., "Inorganic Polymers", Chapters 6 and 7, Academic Press, New York (1962).
3. Rochow, E. G. and Minne, R., J. Am. Chem. Soc., 82, 5625 (1960).
4. Cheronis, N. D., U.S. 2,564,764 (1951); U.S. 2,579,416 (1951); U.S. 2,579,417 (1951); U.S. 2,579,418 (1951).
5. Breed, L. W., Elliot, R. L. and Ferris, A. F., J. Org. Chem., 27, p. 1114 (1962).
6. Aylett, B. J. and Burnett, G. M., Abstracts of International Symposium on Inorganic Polymers, 18-21, July, 1961.
7. Rochow, E. G., U.S. 2,352,974 (1944).
8. Korshak, V. V., Polyakova, A. M., Sakhorova, A. A., Mironov, V. F. and Chernyshev, E. A., Vysokomolekulyarnye Soedineniya, 2, 1370 (1960).
9. MacFarlane, R. and Yankura, E. S., Contract No. DA-19-020-ORD-5507, Quarterly Report No. 7, Naugatuck Division of U. S. Rubber Co.
10. Hopf, H. and Egli, R., Kunststoffe-Plastics, 6, 433-331 (1959).
11. Elliot, R. L. and Breed, L. W., Am. Chem. Soc., Polymer Preprints, 5, p. 587 (1964).

REFERENCES (Cont'd.)

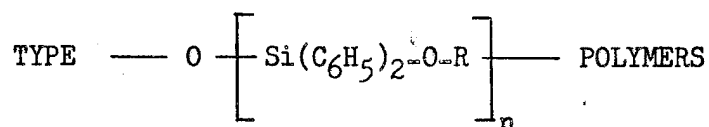
12. Curry, J. E. and Byrd, J. D., J. of Applied Polymer Sci., 9, pp. 295-311 (1965).
13. Unpublished work, Battelle Memorial Institute.
14. Anderson, H. H., J. Am. Chem. Soc., 73, p. 5802 (1951).
15. Larsson, E. and Smith, B., Acta Chemica Scandinavia, 3, pp. 487-492 (1949).
16. Benkeser, R. A., Robinson, R. E. and Landesman, H., J. Am. Chem. Soc., 74, p. 5699 (1952).

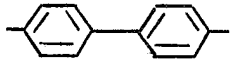
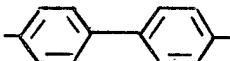
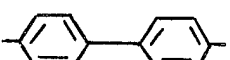
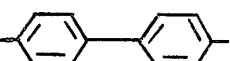
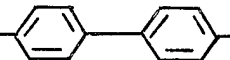
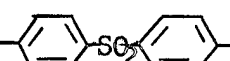



TABLE I

PROPERTIES OF SILANE MONOMERS

<u>Monomer Number</u>	<u>Structure</u>	<u>M.p.</u>		<u>% C</u>	<u>% H</u>	<u>% N</u>
I	$(C_6H_5-NH)_2Si(C_6H_5)_2$	166-167 C	Calculated:	78.65	4.95	7.66
			Found:	78.78	5.23	7.92
II	$(C_6H_5-NH)_2Si(CH_3)_2$	59- 60 C	Calculated:	69.30	7.40	11.55
			Found:	69.10	7.55	11.49
III	$(C_6H_5O)_2Si(C_6H_5)_2$	64- 65 C	Calculated:	78.25	5.47	-
			Found:	78.14	5.23	-
IV	$(C_6H_5O)_2Si(CH_3)_2$	132 C/4.8 mm (B.p.)	Calculated:	68.86	6.59	-
			Found:	69.15	6.39	-

TABLE II

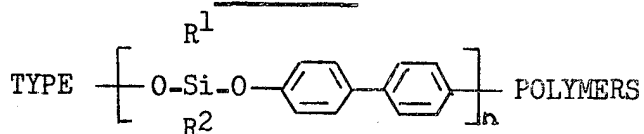


Silane Type	R	Polymerization Conditions		Polymer Softening Temp. °C	M _w
		Time, hrs	Temp. °C		
A		2	300	> 300	—
A		2	300	150-155	81,000
B		5.5	200-300	145-150	38,000
A		2	200	135-140	28,000
B		2.5	250	115-120	16,000
A		1	250	130-135	6,000
A		6	250	65- 70	24,000
B		2	250	65- 70	13,000
A		6	250	65- 70	30,000

A = Dianilino

B = Diphenoxy

TABLE III

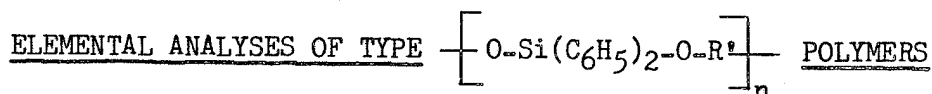


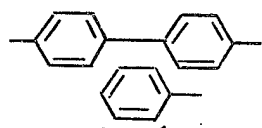
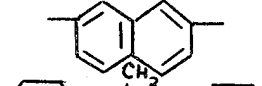
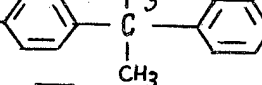
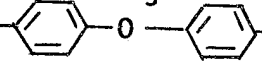

Silane Type	R ¹	R ²	Polymerization Conditions		Polymer Softening Temp, °C	M _w
			Time, hrs	Temp, °C		
A	C ₆ H ₅ -	C ₆ H ₅ -	2	300	150-155	81,000
B	C ₆ H ₅ -	C ₆ H ₅ -	5.5	200-300	145-150	38,000
A	C ₆ H ₅ -	CH ₃ -	2	250	100-105	29,000
A	C ₆ H ₅ -	CH ₃ -	0.5	200	90- 95	9,000
A	CH ₃ -	CH ₃ -	2	250	125-130	35,000
A	CH ₃ -	CH ₃ -	1	250	85- 90	27,000
B	CH ₃ -	CH ₃ -	5	225-300	30- 35	6,000

A = Dianilino

B = Diphenoxy

TABLE IV



R ⁰	Calculated			Found		
	C, %	H, %	Si, %	C, %	H, %	Si, %
	78.65	4.95	7.66	78.13	4.94	8.7
	74.45	4.86	9.67	74.45	4.86	10.56
	77.75	4.71	8.20	77.67	4.74	9.92
	79.37	5.92	6.88	78.41	5.94	7.10
	75.33	4.74	7.34	75.46	4.67	7.96

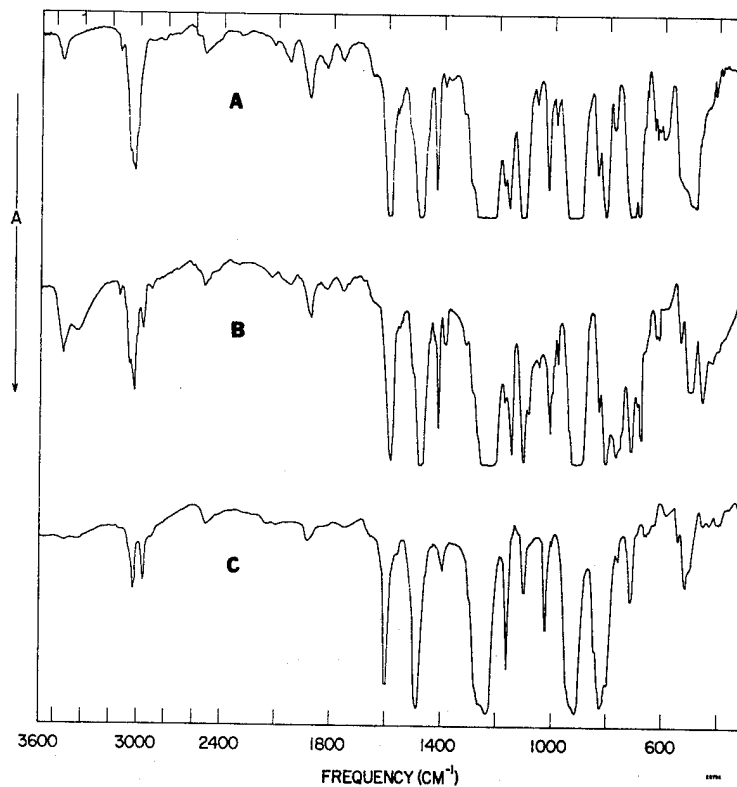


FIGURE 1. INFRARED SPECTRA OF POLYARYLOXYSILANES CONTAINING BIPHENYL AND DIPHENYLSILYL (A), METHYLPHENYLSILYL (B), AND DIMETHYLSILYL CHAIN UNITS (C).

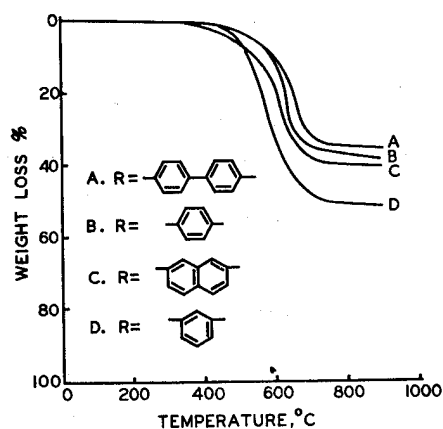
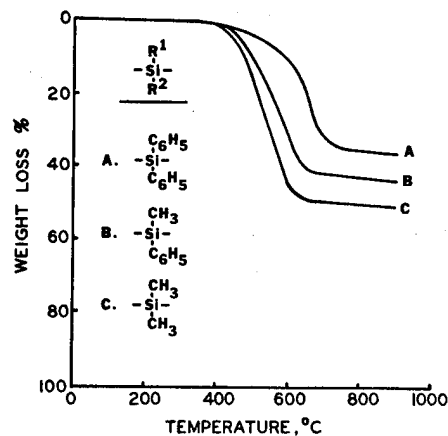


FIGURE 3. THERMOGRAVIMETRIC ANALYSES OF TYPE $[-O-Si(R)_2-O-C_6H_4-C_6H_4-]_n$ POLYMERS UNDER NITROGEN AT A HEATING RATE OF 4 °C/MINUTE

FIGURE 2. THERMOGRAVIMETRIC ANALYSES OF TYPE $[-O-Si(C_6H_5)_2-O-R-]_n$ POLYMERS UNDER NITROGEN AT A HEATING RATE OF 4 °C/MINUTE



8970-4
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PARYLENE - A NEW THIN FILM INSULATING MATERIAL

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A new polymer, based on poly(p-xylylene) and which is capable of forming extremely thin films, has been developed by the Plastics Division of Union Carbide. Called "paylene", the new material is deposited from the vapor phase by a process which in some respects resembles vacuum metallizing. Although a number of other methods have been suggested for depositing organic materials by vacuum techniques, namely, by glow discharge,¹ ultraviolet irradiation,² and electron bombardment,³ these all involve external stimulation of the monomer. The parylenes, whose preparation and properties are described in this article, do not require activation or catalysis of the growth step.

The main chemical steps involved are shown in Figure 1, as well as the process in block form. Di-para-xylylene, "DPX", a white, stable, crystalline solid, melting at 280°C., is the key intermediate. This material can be sublimed under vacuum (about 1 mm Hg) at 200°C., giving rise to the corresponding vapors. As these vapors enter the pyrolysis, or cleavage zone, maintained at about 600°C., they are cleaved, specifically at the two methylene-methylene bonds, to give a nearly quantitative yield of monomeric para-xylylene. Para-xylylene is an unusual molecule in that it is extremely reactive in any condensed phase, but is relatively stable in vacuum, even at 600°C. In fact, when adsorbed on surfaces, para-xylylene behaves chemically as if it were a diradical with one unshared electron on each methylene carbon.

As the vapors of para-xylylene pass through the cleavage zone and into the cooler deposition zone, generally held at room temperature, the molecules tend to become adsorbed on the surfaces of solid substrates. Because of the reactivity of the monomer, polymerization occurs simultaneously with adsorption, and no intermediate phase is ever isolated. Conversion of monomeric para-xylylene to polymer is quantitative, so, in essence, DPX is converted to polymer in 100% yield. Of course, the deposition efficiency, i.e., the percent of DPX which appears as polymer on the desired substrate, is never 100%, but, by careful selection of conditions and control of the process, efficiencies in excess of 90% may be achieved.

The process, then, consists of three steps - sublimation of the dimer, cleavage or pyrolysis giving monomeric para-xylylene, and deposition or polymerization. A necessary fourth component in this system is the vacuum pump and associated protective traps.

It is noteworthy, as mentioned above, that activation of the monomer is not

necessary, and that the monomer as produced in the cleavage step is already extremely reactive. Furthermore, such "activation" as occurs during the formation of monomer is isolated, both chemically and spatially, from the deposition zone where polymerization and growth take place. Neither the substrate nor the polymer after it is deposited is subjected to any energetic bombardment. This, plus the fact that xylylene is a specific chemical entity and not a mixture of ions, radicals, and unactivated monomer are primarily responsible for parylene being a true linear homopolymer. In addition, kinetic studies indicate that every monomer molecule can both initiate new chains or add to chains already growing. The growth step, shown in Figure 2, may be represented as addition of a highly reactive vinyl monomer to an active chain end. The polymerization rate, and hence the coating thickness, is determined by only two parameters - substrate temperature and xylylene pressure. In Figure 3, the growth rate is shown as a function of pressure for several substrate temperatures. Rates as low as 100 Å per minute and as high as one mil (over 250,000 Å) per minute, have been measured. Film thicknesses from under 100Å up to 50 mils can be obtained which, depending on substrate preparation and cleanliness, are apparently pin-hole free over relatively wide areas, even in the 1000Å range.

The polymer shown in Figure 4, Parylene C, has one hydrogen atom on the ring substituted by chlorine. Parylene D, with two chlorine atoms per ring is also indicated. These polymers are made by the same sequence of sublimation, cleavage and deposition as used for the unsubstituted polymer, Parylene N. The corresponding dichloro- and tetrachloro-dimers are made using more or less conventional routes from DPX. More than twenty additional derivatives of DPX have been made in the laboratory and have been similarly converted to polymers.⁴ These include the other halides, alkyls, acyl and carboalkyl compounds. Each polymer has its own set of physical, electrical and thermal properties. Of the three polymers now available, Parylenes N, C and D; N has the best electricals; C the best physical and barrier properties, and D the best thermal and electrical resistance. Considering the broad range of polymers and properties conceivable, the parylenes indeed represent a new family of plastics.

The physical and thermal properties of Parylenes N and C are summarized in Table I. First of all, the molecular weight of both polymers is about 500,000. This is very high, especially considering that it represents a number average molecular weight. Because of the high molecular weight and because the melting temperatures and crystallinity are high, Parylenes N and C cannot be formed by conventional methods such as extrusion or molding. Solubility in organic or other media is low so that generally they cannot be formed by casting. The parylenes are soluble, however, in solvents such as α -chloronaphthalene at 250°C., showing that they are true linear polymers.

Although not shown in the table, pendulum impacts are in the 30 to 60 psi range, values intermediate between brittle polymers and truly tough materials such as polyethylene and polycarbonate.

The high melting point, over 400°C. for Parylene N, would generally indicate high end-use temperatures. This is the case where the polymers are protected from oxygen. Continuous use temperatures of 220°C. for ten years are estimated by extrapolation of Arrhenius-type plots. Hermetically sealed packaging is common in the electronics industry, and a good measure of protection is obtained merely by potting the parylene-coated part in phenolic molding compounds.

In the presence of air the methylene groups on the polymer are attacked by oxygen, resulting in random scission of the polymer backbone. This eventually leads to a decrease in tensile strength, although electrical properties are main-

tained for a longer period of time. The temperatures at which the polymers can be used in air for various lengths of time are shown in the table.

The parylenes have superior toughness at cryogenic temperatures; supported films have withstood Gardner falling-ball impact tests of over 100-inch pounds at -196°C . When deposited on various metals, the polymers, when cycled to -269°C ., did not crack, peel from the substrate, or show any change in electrical properties.

Barrier properties are given in Table II. Parylene C, particularly, is an excellent barrier to the permanent gases and to moisture vapor. This is probably enhanced by the fact that contact with the substrate is better than other plastics, by virtue of its being applied by vapor deposition. This is emphasized in a photomicrograph of a Parylene C replica of a polyethylene single crystal. The crystals were sprayed on a glass microscope slide, the slide coated with Parylene C, stripped off, the polyethylene dissolved in hot hexane, the parylene replica shadowed by low-angle metal evaporation, and the replica then photographed in an electron microscope. The actual size of the crystals are about 5 microns and each step in the spiral dislocation is of the order of 100\AA in height. This demonstrates the fidelity of the coating technique and the ability to cover complex shapes with a uniform film under very mild conditions. The substrate need only withstand the conditions of vacuum at room temperature and comes in contact only with the monomer vapor or the polymer resulting from it.

In addition to being "resistant" to gases and moisture, the parylenes are resistant to permeation by organic liquids and reagents. Aromatic hydrocarbons penetrate faster than other solvents. The parylenes are resistant to attack by acids, bases, oxidizing agents and reducing agents. Parylene N is attacked slowly by cold fuming nitric acid and by hot concentrated sulfuric acid. This rate of attack is much slower in the chloro-substituted parylenes.

The electrical properties are given in Table III. The high dielectric strength and volume resistivity, coupled with the low dissipation factor, plus the fact that the dielectric constant and dissipation factor change only slightly within a wide range of temperature and frequency, make Parylene N an outstanding capacitor dielectric. The ability to manufacture films thinner than other polymeric dielectric materials enables construction of capacitors with five and twenty times greater volumetric efficiency.

REFERENCES

1. Goodman, J., J. Polymer Sci., 44, p. 552 (1960).
2. Gregor, L. V. and McGee, H. L., Proc. Fifth Annual Electron Beam Symposium, Alloyd Corp., Cambridge, Mass., 1963.
3. Christie, R. W., J. Appl. Phys., 31, 1680 (1960).
Haller, I. and White, P., J. Phys. Chem., 67, 1784 (1963).
4. Gorham, W. F., paper presented at April meeting of American Chemical Society, Detroit, Michigan, April 1965.

TABLE I

PHYSICAL PROPERTIES OF PARYLENE AND OTHER POLYMERS

<u>Properties</u>	<u>Parylene N</u>	<u>Parylene C</u>	<u>PE Terephthalate</u>	<u>TFE Resin</u>
Secant modulus, 1% strain, psi	350,000	400,000	650,000	85,000
Tensile strength, psi*	9,000	13,000	26,000	3,400
Elongation to break, %*	200	200	170	300
Density, gm/cc	1.103-1.120	1.289	1.397	2.16
Index of Refraction	1.669	1.629	1.50-1.57	
T(melting) °C**	410	275-295	260	330
T(glass, transition) °C**	60-80	80-100	95-105	-125
T ₅ (where modulus = 100,000) °C**	165	125	130	10
T ₄ (where modulus = 10,000) °C**	-	250	245	195
Temperatures, °C, at which polymers have a useful life of				
inert (1 hour	350	260		
atmos-(1000 hours	270	260		
phere (10 years***	220	235	125	280
(1 hour	150	170		
air (1000 hours	95	115		
(10 years***	65	90	125	250

*Measured at 10% strain/minute

**Taken from secant modulus-temperature curve

***Extrapolated

TABLE II

BARRIER PROPERTIES OF PARYLENE AND POLYMER FILMS

<u>Polymer</u> <u>2-mil Films</u>	<u>Gas Permeability</u> <u>cc/mil/100 in 2/24 Hrs.</u>			<u>Moisture Vapor</u> <u>Transmission</u> <u>5/mil/100 in 2/24 Hrs.</u>
	<u>N₂</u>	<u>O₂</u>	<u>CO₂</u>	
Parylene N	9	30	225	14
Parylene C	0.7	5	12	1
Polyvinylidene Chloride	0.2	1.0	3.8	1
Polyethylene Terephthalate	1.0	1.8	25	3
Polyethylene	135	350	1400	21
Polytetrafluoroethylene	290	770	1835	3
Polystyrene	40	200	900	120

TABLE III

TYPICAL ELECTRICAL PROPERTIES OF PARYLENE AND OTHER POLYMERS

(Tests conducted on 3-mil films)

<u>Property</u>	<u>Parylene N</u>	<u>Parylene C</u>	<u>PE Terephthalate</u>	<u>TFE Resin</u>
Dielectric strength, ST, volts/mil	6500	3700	-	-
Corrected to 1/8"	700	520	780	480
Dielectric strength, step by step, volts/mil	6000	1200	-	-
Corrected to 1/8"	550	410	510	430
Volume Resistivity, at 23°C, ohms	1.4×10^{17}	8.8×10^{16}	1.6×10^{16}	2.8×10^{16}
Surface Resistivity, 23°C, 50% RH, ohms	10^{13}	10^{13}	-	-
90% RH, ohms	9×10^{11}	7×10^{11}	10^{12}	3×10^{12}
Dielectric constant				
60 cps	2.65	3.1	3.27	2.08
1 K cps	2.65	3.1	3.27	2.08
100 K cps	2.65	3.0	3.19	2.08
1000 K cps	2.65	2.9	-	2.08
Dissipation factor				
60 cps	0.0002	0.02	0.00145	0.00012
1 K cps	0.0002	0.0195	0.00424	0.00013
100 K cps	0.0004	0.0156	0.0163	0.0004
1000 K cps	0.0006	0.0128	-	0.0005

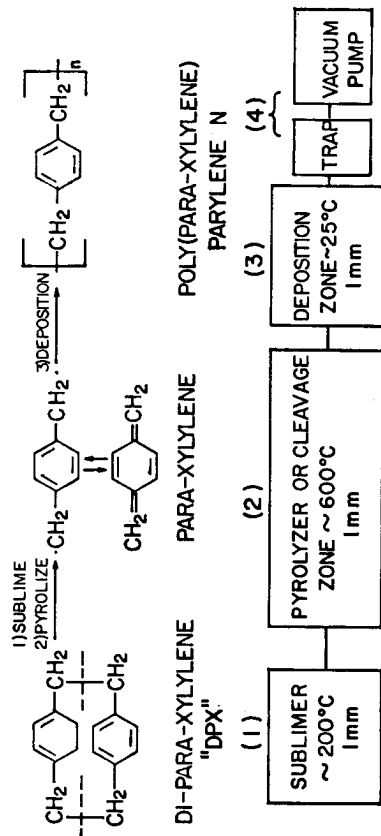


FIGURE 1

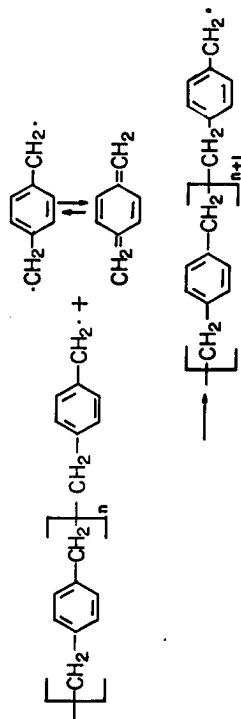


FIGURE 2

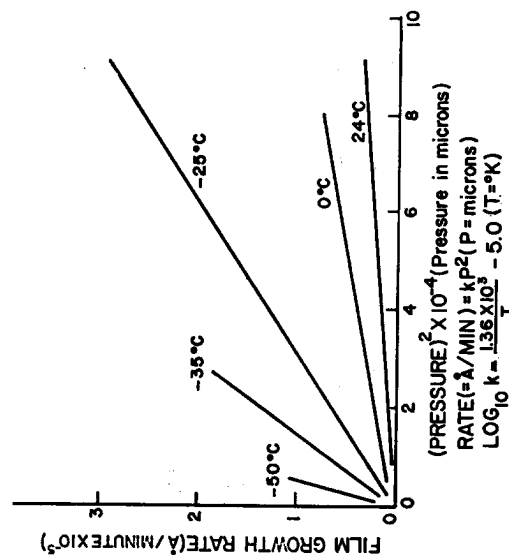


FIGURE 3

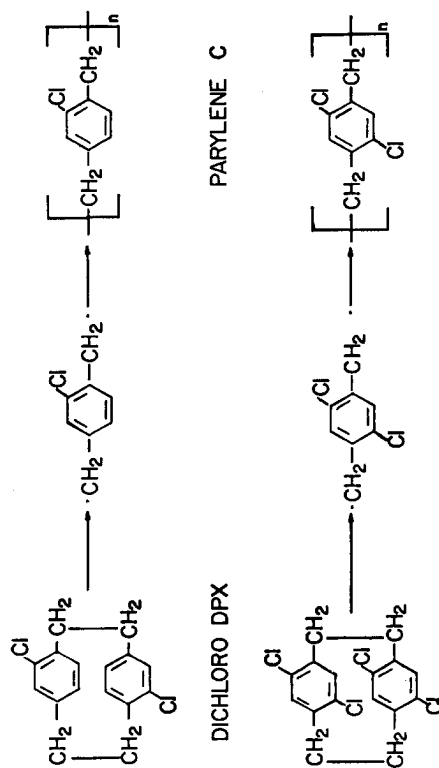


FIGURE 4

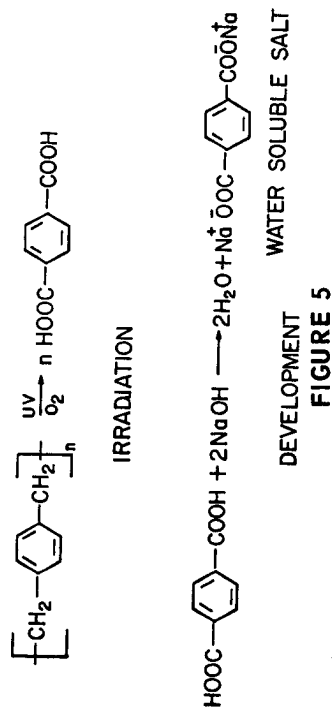


FIGURE 5

HEAT RESISTANT GLASS REINFORCED COMPOSITES BASED ON POLYIMIDE
AND DIPHENYL OXIDE COMPOSITES

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ABSTRACT

[This paper discusses two new classes of resins, namely, polyimides and diphenyl oxides, which show promise for heat resistant reinforced plastics applications. These resins were selected as a result of a preliminary evaluation and screening program consisting primarily of 600°F heat aging studies on glass fabric reinforced laminates, and involving a number of new and potentially heat resistant resin systems. Laminates based on the diphenyl oxide material were found to offer a service life on the order of 200 hours @ 600°F; whereas the polyimide laminates provided superior strength retention after 1000 hour aging @ 600°F.] These materials appear to fill the existing requirement for improved heat resistant plastics systems for missile and advanced aircraft applications.

In order to utilize these materials in applications work, it was necessary to develop and optimize fabrication processes, and to generate engineering properties data.

[Problems in fabricating composites from these resins arise from the high cure temperatures required, and the release of volatile materials during cure. Process studies have been undertaken on each of the systems, and production-oriented techniques have been developed for producing high quality composites. Fabrication methods include press molding, autoclave and vacuum bag molding, and filament winding.]

INTRODUCTION

The use of reinforced plastics for aircraft and aerospace applications has increased steadily in recent years, as a result of their unique structural and fabrication properties. With the advent of advanced flight vehicles, such as the supersonic transport, comes a requirement for materials which will resist prolonged exposures to temperatures in excess of 500°F. Standard commercially available plastics, such as phenolic, epoxy, or epoxy-novolac based composites will not withstand these extreme temperature environments for extended periods; therefore, intensive research has been directed toward the development of improved heat resistant polymers.

A program was funded by the Air Force Materials Laboratory to evaluate and screen several of the available new and potentially heat resistant resin systems, and to develop processing information and design data on the most promising candidate materials. This program also provided for the construction of subscale prototype structures to prove-out the applicability of both the materials and processes to production manufacturing techniques. Most of the work discussed herein was performed under this Air Force Program.

EVALUATION AND SCREENING

First efforts were directed toward an evaluation and screening of fifteen candidate resin systems in the form of press molded laminates. Criteria for judging the performance of the laminates were initial flexural strength, and flexural strength retention after various exposure periods at 600°F. Weight loss measurements were also made after each aging period to further indicate the heat aging stability of the materials. Flexural strength as a function of exposure time at 600°F is shown in Figure 1 for five of the best systems investigated. Laminates based on polyimide and diphenyl oxide resins clearly demonstrated superior heat resistance over the other materials tested. Strength retention at 600°F, after 200 hours aging at 600°F, was 70% for the polyimide laminate material, based upon an initial flexural strength of 54,000 psi. Weight loss after aging was measured to be 1%. The diphenyl oxide laminate material retained 43% of the initial 78,000 psi flexural strength, with a weight loss of 6% measured after aging.

Additional heat aging studies were later conducted to include 700 and 800°F exposures, and with aging times extended until the flexural strength tested at aging temperature dropped to approximately 25% of the original R.T.-tested, unaged flexural strength. Figure 2 further illustrates the ability of the polyimide laminate material to withstand prolonged exposures to elevated temperatures. Similar aging studies on diphenyl oxide laminates showed excellent strength retention at 400 and 500°F as illustrated in Figure 3.

POLYIMIDE COMPOSITES

Polyimide resins, like the diphenyl oxides, are condensation polymers supplied in a solvent solution; however, the outgassing problem during cure is more severe in the case of the polyimides for two reasons - the amount of condensation products released is greater and high boiling solvents, such as n-methyl pyrrolidone and dimethyl formamide are used in the resin solution. Press temperatures of 500-600°F are required in order to remove the residual volatiles from the prepreg material, and early laminates were generally quite porous with flexural strengths in the range of 35,000 - 55,000 psi.

More recent processing studies have been directed toward low-pressure, vacuum laminating techniques and the results obtained thus far appear extremely promising from the standpoint of ease of fabrication, and reproducibility. This technique provides a practical approach to fabricating complex shapes, and does not require elaborate or costly tooling. Since the vacuum system serves to draw off volatiles, high curing temperatures are no longer required. The fabrication procedure is very similar to that used in conventional vacuum laminating except that more bleeder material is required.

Specifically, this process involves stacking plies of polyimide prepreg material on a vacuum table or mold, and placing a steel bleeder spring around the lay-up. The assembly is then overlayed with silicone treated release fabric and several plies of dry glass fabric. The laminate is then cured under vacuum (10-14 psi) according to a programmed schedule which includes 1-1/2 hours at 350°F. After the initial cure the laminate is postcured 8-10 hours at 550 to 600°F. The postcure schedule will depend upon the end use; however, processing studies have indicated that relatively short periods at elevated temperature are adequate for most applications.

DIPHENYL OXIDE COMPOSITES

The resinous material derived from diphenyl oxide polymerizes upon heating and releases water as the major by-product. Also, the resin is supplied in a 40% solvent solution to facilitate handling during impregnation of reinforcement. Difficulties were encountered in early work due to outgassing during press cure, as evidenced by minute voids within the cured laminate and often blistering during cure and postcure. Variation in the preparation of the prepreg material resulted in substantial improvement. By carefully controlling the B-stage time and temperatures, and subsequently the amount of residual solvent, laminates with a theoretical void content of less than 3% have been prepared.

Laminate process studies were conducted in order to study the effect of variables such as cure temperatures, cure pressures, mode of pressure application, and postcure schedules. Best results were obtained on laminates cured in the press at 320°F, 300 psi for one hour. The laminate is then placed in an air circulating oven, and postcured to provide maximum strength at elevated temperature. Postcure schedules will vary with application and part thickness; however, it should include the maximum temperature to be encountered in service or test conditions. A typical schedule for 1/8" thick laminates for 500-550°F heat resistance would be 24 hours at 250, 300, 350, 400, 450, 500 and 550°F. Shorter times at these temperatures have been successfully employed; however, physical properties will drop after initial exposures to elevated temperatures, and then tend to increase with temperature exposure due to the postcure effect.

An alternate fabrication method involves the use of the vacuum bag technique with an oven cure; or preferably, cure in an autoclave under augmented pressures. This technique is recommended in cases where press curing is impractical from the standpoint of economics, or due to the shape of the article to be fabricated. This process consists of laying up the composite to the desired thickness and configuration, and overlaying the assembly with a bleeder material such as silicone treated glass fabric. Vacuum is then applied and the composite oven cured, or autoclave cured (50-100 psi) to 300°F. The composite structure is then placed in an air circulating oven for postcure.

FILAMENT WINDING

Both diphenyl oxides and polyimides have been used successfully in the preparation of wound composites. The majority of work has involved specimens of the N.O.L. ring configuration, although flat panels and cylinders have been constructed.

Filament wound subscale radomes have been fabricated on other programs, and no scale-up problems are foreseen for the production of large filament wound structures. Fabrication procedures are essentially the same as employed using conventional winding materials, although a heat gun is required during winding to soften the prepreg roving, thereby providing improved fiber compaction. Curing under vacuum is desirable to aid in the removal of volatile materials. Table I reports data on polyimide and diphenyl oxide N.O.L. rings prepared with E glass roving.

GLASS FINISHES

Several commercially available glass finishes have been evaluated in combination with diphenyl oxide and polyimide resins. In short, these studies have shown that A-1100 finish is as good as any and better than some for service in the 600°F range; however, none provide the needed heat resistance for long term exposures. Improved heat resistant finishes and glass-to-resin coupling agents are required if maximum properties are to be obtained using these new resin systems.

SUMMARY

The ultimate objective of the work described in this discussion was to provide a new and improved reinforced plastics system for use at elevated temperatures. Both reinforced diphenyl oxide and polyimide-based composites were developed to the point that they may now be considered for applications work, with a reasonable degree of reliability regarding both properties and processability. These materials now make possible the use of reinforced plastics for certain applications which could not have been considered using conventional plastics systems.

TABLE I

TYPICAL PROPERTIES OF FILAMENT WOUND NOL RINGS PREPARED WITH POLYIMIDE

AND DIPHENYL OXIDE RESINS AND E GLASS ROVING

Material	Hoop Tensile Strength, psi		Horizontal Shear Strength, psi	
	R. T.	600°F hrs. @ 600 F	R. T.	600°F hrs. @ 600°F
Polyimide/E Glass	120,000	91,000	3,300	4,300
				4,200
Diphenyl Oxide/E Glass	170,000	106,000	8,600	3,000
				2,800

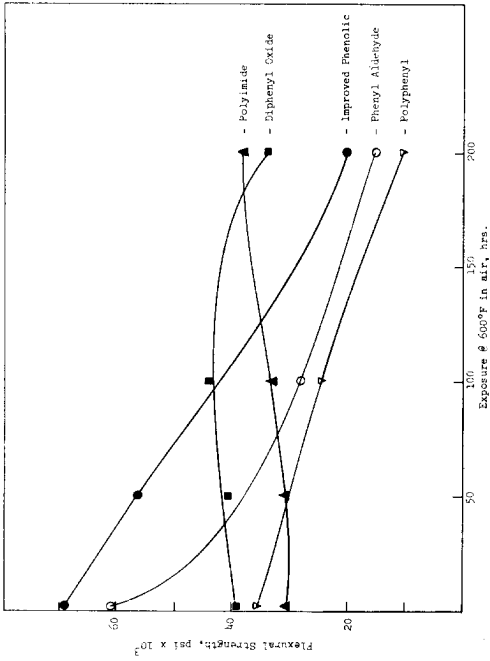


FIGURE 1: 600°F Flexural Strength as a Function of Time @ 600°F for Various Laminates (Screening Program)

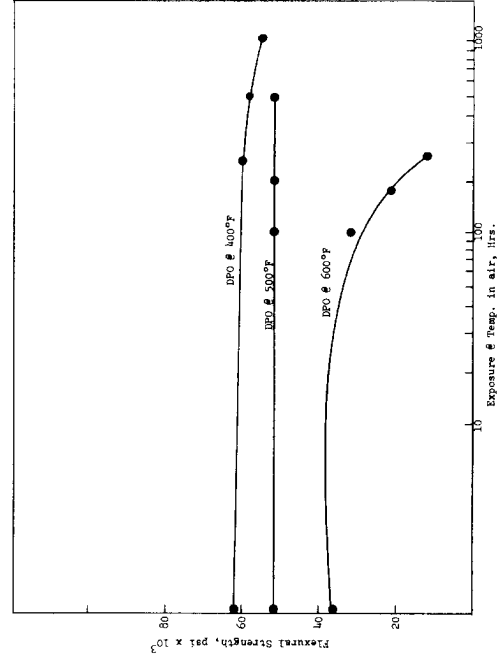


FIGURE 3: Flexural Strength of Diphenyl Oxide Laminates as a Function of Time @ 400, 500, & 600°F, Tested @ Aging Temperature

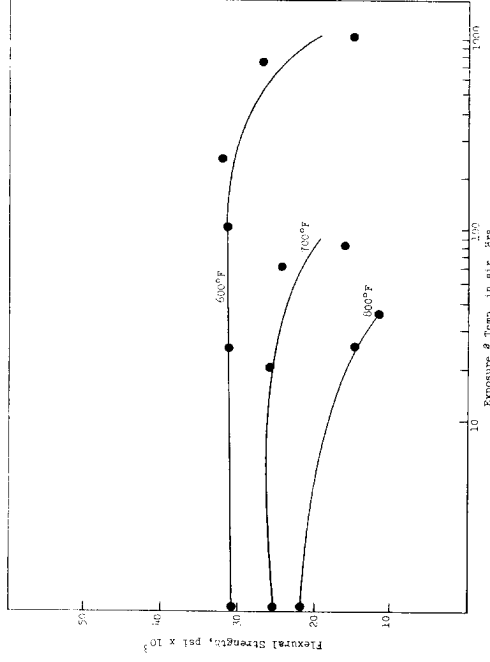


FIGURE 2: Flexural Strength of Polyimide Laminates as a Function of Time @ 600, 700, & 800°F, Tested @ Aging Temperature

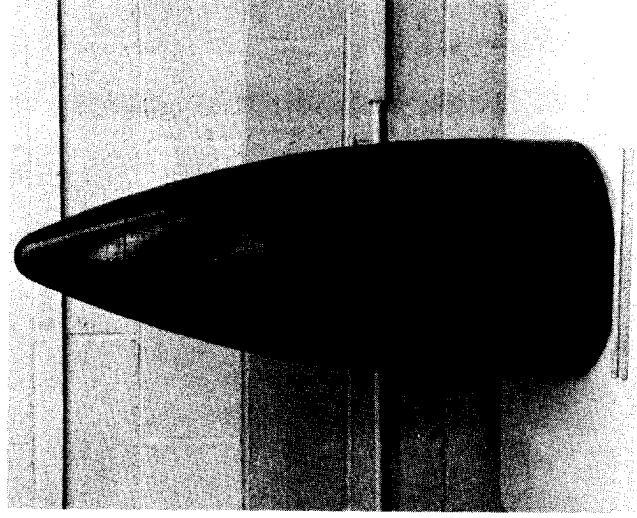


FIGURE 4: Radome Fabricated from Polyimide Resin and Glass Fabric

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MOLDED AIRCRAFT WHEELS OF EPOXY RESIN REINFORCED
WITH NONCONTINUOUS GLASS FILAMENTS

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INTRODUCTION

Aircraft wheel design has developed over the years into a field of highly refined material application. Wheel assemblies are fabricated with materials having widely varying properties. Operating conditions imposed on wheel assembly components are so severe that subtle differences in material properties (e.g., rate of heat transfer) can govern material selection for a particular wheel application. For example, high-energy brake disks generate such heat to the tire through conventionally fabricated wheel assemblies that tire failures have resulted on certain aircraft. One Goodyear approach to solving this problem used high-temperature-resistant reinforced plastics possessing better heat transfer characteristics than candidate metals.

The most widely used materials for aircraft wheel construction at present are cast magnesium and forged aluminum. In spite of value proven in many years of successful operation, these materials still admittedly have characteristics that reduce durability and safety. Cast magnesium wheels are highly susceptible to corrosion, particularly in a salt water environment, and are limited by temperature under high stress conditions. These wheels also have a relatively low strength-to-weight ratio. Forged aluminum shows many improvements over cast magnesium, but demonstrates a higher rate of heat transfer, rapid crack propagation, and a somewhat higher cost than cast magnesium.

Analysis of cast magnesium and forged aluminum properties indicated that molded reinforced plastics might offer a successful alternate wheel material. One outstanding incentive was potential reduction in costs of wheel replacement forced by corrosion. Other factors recommending reinforced plastics in wheel applications included their high strength-to-weight ratio, superior resistance to crack propagation, and lower rate of heat transfer.

In 1960, Goodyear started a company-funded development program to demonstrate potentials of the reinforced plastics aircraft wheel. Some of the salient achievements resulting from this work are described in the following section.

DEVELOPMENT AND TESTING

A. Testing Available Materials

The Goodyear organization began its corporate-funded development of reinforced plastics aircraft wheels by selecting and testing various candidate materials. Commercially available materials with the best properties according to available data were tested. The company fabricated a mold to form wheel halves for a 6.00-6 auxiliary wheel. This wheel is shown in Figure 1. The most promising materials were molded into parts that were checked for strength in a "burst" test. In this test a tire mounted on test assemblies was inflated with noncompressible fluid to a pressure sufficient to cause rim failure.

The test eliminated all but one commercially available material as a contender for the plastics wheel. High material cost provided an incentive for continued company research.

B. Development of Molding Compounds

After testing available materials, Goodyear engineers decided the only alternatives remaining were either to develop a new molding material or to alter an existing commercial material. Goodyear began development work with polyester molding compounds. After thorough investigation of properties in the family of polyesters, the company shifted its research to epoxy systems using noncontinuous fiberglass reinforcements. Investigation determined that epoxies held the real promise for providing necessary wheel strength. This investigation produced a material containing approximately 60% one-inch fiberglass strands and reaching 40,000-50,000 psi tensile ultimate when molded into 1/4 in. thick flat panels.

C. Investigation of Existing Materials

Concurrently Goodyear investigated unidirectional fiberglass filaments preimpregnated (prepreg) with resin and cut to short lengths for molding. Physical strengths developed in this material for the filament-wound Polaris rocket motor case made it particularly attractive. The material consists of E-787^a epoxy resin matrix reinforced with S-glass rovings.

Remnants of Polaris prepreg roving cut manually to one-inch lengths produced sufficient material to mold small test panels. The first attempt at molding the material proved most discouraging. The material's extreme temperature sensitivity caused many molding problems. Molded under relatively low pressure, the panel was squeezed dry of resin. Remaining material aged approximately two weeks at room temperature before another molding attempt was made. This time the sample was suitable for testing. Tensile tests of this panel also yielded results in the 40,000-50,000 psi range. The apparent ease of handling a prepreg material compared with problems of developing a new Goodyear compound convinced investigators the company should concentrate on altering existing molding materials.

^aA designation of U. S. Polymeric Chem., Inc., Santa Ana, Calif.

D. Fiber Cutting Problems

The decision to proceed with prepreg roving made fiber cutting the next problem to be studied. Goodyear tried to obtain material in short lengths from the supplier. The supplier's inexperience in this particular material application resulted in a compound aged well beyond the state required for satisfactory molding. Need for control of resin aging advancement made it necessary to cut the fibers to length at Goodyear.

Several types of fiber cutters were tried unsuccessfully before a suitable design was evolved. The company conceived a relatively simple design to cut the fiber at a rate of 0.1 lb. per min. per roving strand fed into the machine. The machine's maximum output was 1.2 lb. per min. of one-in. cut fibers. The fiber cutter incorporated a carbide-tipped rotating cutter blade that sheared the fiber against a stationary carbide-tipped blade (Figure 2). The roving strands were fed into the cutter by geared teflon feed rolls. The carbide cutter speed was constant. Modifications have been made to the metering rolls, which now permit their speed to be changed relative to the cutter blade, thus cutting fibers to predetermined lengths from 1/16 in. to 1 in.

E. Material Aging Discoveries

1. Effects of Aging on Cutting

Since resolving the mechanical problems of cutting the prepreg roving, much has been learned about the aging requirement prior to cutting. For optimum molding results and for ease in handling after cutting, the roving must be free of tack. Excessive aging of the impregnating resin will cause feathering of the cut, but material cut at the proper stage will form a distinct fiber bundle clean at both ends without feathering. The bundle will remain loose and free of other bundles stored in the same container.

2. Aging Controls

Controlled aging is the next step in preparing cut fibers for molding. The material was molded successfully for the first time after approximately two weeks of room-temperature aging. At present no way has been found to accelerate aging by elevating temperatures while retaining comparable molding results. Material has been molded successfully after 48 days of aging assisted by preheat operations. As room temperature aging time increases, it is necessary to decrease preheating and to increase molding pressure. The lowest molding pressure used successfully was 1000 psi and the highest was 3000 psi for 48-day material.

3. Statistical Standards for Aging

Experience in molding techniques gained in development of Polaris-type cut roving materials has moved the process at Goodyear from the category of art to one having statistical standards for satisfactory molding. Until recently the

skill of the press operator or process specialist in selecting the proper process corrective measures meant the difference between success and failure in wheel molding. Restrictions imposed on the molding process by material shelf life and temperature sensitivity have been relieved. Goodyear has developed a background of molding cycles information describing material age condition, preheat time and temperature, mold temperature, cure time, and molding "bumping". This background provides a statistical standard. Principal factors contributing to difficulty in processing the material probably are the high fiberglass content (about 80%), the absence of fillers and flow-control agents and viscosity of the epoxy resin system. There is no doubt that with proper care the material can be molded into parts having exceptional mechanical properties.

F. Testing of E-787 Resin System

1. General

Goodyear extensively tested the E-787 resin system using 20 end (204 strands each of fiberglass filament) high tensile strength (HTS) finish S-glass roving to determine its mechanical properties when used in various fiber lengths.

The accompanying graph (Figure 3) shows the relationship existing between fiber length and ultimate tension, compression, and flexural strengths. Also of great interest are the exceptional results on modulus (Figure 4). Impact strength and notch sensitivity are shown in Figure 5. All results shown are based on net molded specimens.

Alignment of longer fibers in the molded specimens greatly improved the material properties. The same alignment occurs to some degree in parts compression-molded from the material.

2. The Burst Test

Goodyear based evaluation primarily on functional tests of molded parts^a. Initial laboratory qualification tests were based on potential use of a 6.00-6 auxiliary wheel mounted on a helicopter. The first test used was the inflation or "burst" test. In evaluation of moldings from cut Polaris-type material the tires in some trials left the rims before the plastics wheel failed. Normal burst-test requirement is three times the standard inflation pressure of 82 psi. At 300 psi the qualification test unit failed (Figure 6).

3. Dynamometer Test

The second test, judged the most critical for the molded plastics wheel, was the roll test (Figure 7). In this

^aMIL-W-5013E: Wheel and Brake Assemblies, Aircraft; 20 December 1960.

test a dynamometer was accelerated to 30 mph surface speed. At that speed the wheel assembly was "landed" against the dynamometer with the rated load of 3900 lb. until the dynamometer slowed to a stop. The wheel then was retracted from the dynamometer which was once again accelerated to 30 mph. This dynamometer test was recycled repeatedly in an attempt to cause wheel failure. The minimum requirement for the wheel is 250 mi of roll at 3900 lb. The wheel molded from the one-in. cut roving endured more than 2000 miles at rated load without failure before being removed from the dynamometer test.

4. Axial Test

The third was an axial or side load test (Figure 8). A wheel was mounted on an axle and a side load applied to the tire. The wheel must withstand a sideward load of 4875 lb. (1.25 times the rated load of 3900 lb.). This proof-test load was held for 10 sec. before the load was raised in an attempt to force wheel failure. The plastics wheel was loaded to 8100 lb. without failure.

5. Radial Loading

The final qualification test was radial loading (Figure 9). A wheel assembly was mounted in its normal position on an axle with a dead load applied to the tire in the radial direction. The required proof-test load of 9750 lb. was held for 10 sec. The load was then increased to attempt failure. The tire flattened on the load side until the load was borne by the rim of the plastics wheel. The test load was raised to 17,500 lb. without wheel failure.

A later test to 28,000 lb. caused hub failure. Another test was added beyond the qualification requirements to check for creep of the plastics material. In this test a wheel assembly was held under the rated radial load for 60 days with the wheel inspected at 30-day intervals for permanent set. After 60 days no permanent set was detectable.

TEST RESULTS AND CONCLUSIONS

A. General

The qualification tests generally proved two points - that a molded plastics wheel could pass all the test requirements and that the wheel design stress level selected was unnecessarily low. After evaluating these test results, Goodyear designed and fabricated a larger size plastics helicopter wheel (6.50-10) (Figure 10). This wheel passed all its qualification tests with ease. This wheel assembly incorporated a disk brake, which added the requirement for heat resistance to 250°F.

B. Failure Experiences

The first wheel assemblies using the E-787 resin system were delivered in 1963. To date, Goodyear has recorded only two wheel failures. In one, a helicopter equipped with the plastics wheels was taxiing at approximately 30 mph when it was taken through an abrupt 90° turn. The tire separated from the wheel. The helicopter weight impact on the plastics wheel damaged the bead flange. In pilot-training maneuvers, a helicopter was taxied around the runway for a prolonged period under partial braking. The heat generated was judged in excess of 600°F in the wheel flange. A tire mounted to a metal wheel subjected to these heating conditions would have failed earlier because of greater heat conductivity. The plastics wheel was damaged beyond further use by carbonizing of the bonding resins. Both failures were judged to be the results of excessive abuse of the wheels with no adverse reflection upon the wheel designer or fabricator.

C. Future of High Performance Molded Plastics

The main problem confronting manufacturers in production of plastics wheels has been high cost. The material used for these parts beyond question has high quality. Considering successful application in Polaris motor cases, Goodyear has used every effort to find the ultimate in material performance from the bare fiberglass as well as the impregnating resin system. This has placed Goodyear's plastics wheel program in an unfavorable cost position compared with the conventional magnesium and aluminum fabrication materials. Plastics traditionally are considered a low-cost serviceable substitute for metal in parts manufacturing. In the market place consumers have become so indoctrinated with this philosophy that they expect plastics prototypes to be cheaper than the metal originals. Aluminum is now a fairly common and inexpensive material with much background in time and experience.

[This application of molded reinforced plastics materials to a critical aircraft wheel program must be viewed in a research and development context.] In this context cost effectiveness comparisons to metal counterparts are valid only when production modes and quantities are established to be at a par.

[In the plastics field, Goodyear's plastics wheel program is viewed as progress toward establishing engineering acceptance for plastics. To be considered successful, new materials must promise better performance than traditional metal components. The structural, functional, and growth aspects of molded reinforced plastics makes it a formidable contender in this field. With the technical emphasis presently being placed on new reinforcement and matrix materials by government and industry, it appears inevitable that composite materials like the wheel have a very definite place in the aerospace industry.]

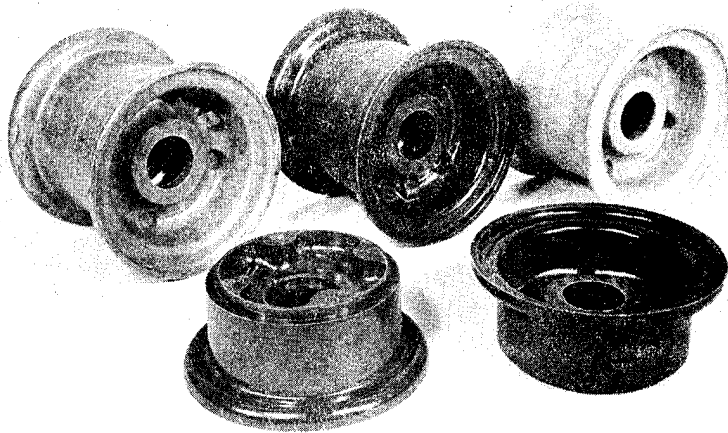


FIGURE 1: Plastic Helicopter Wheels, 6.00 - 6

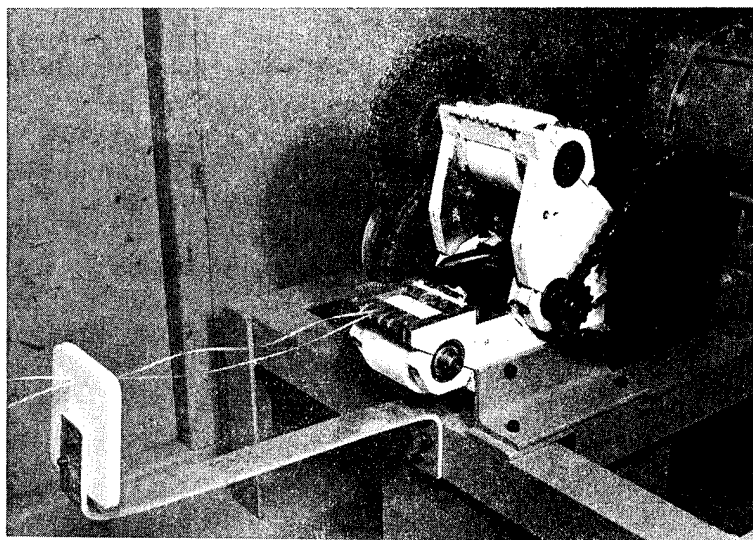


FIGURE 2: Fiber Cutter Device in Open Position

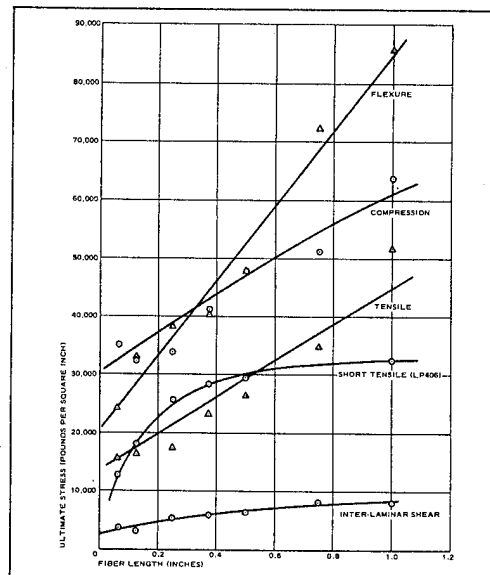


FIGURE 3: Mechanical Properties of Noncontinuous Glass-Reinforced Epoxy Molding Compound

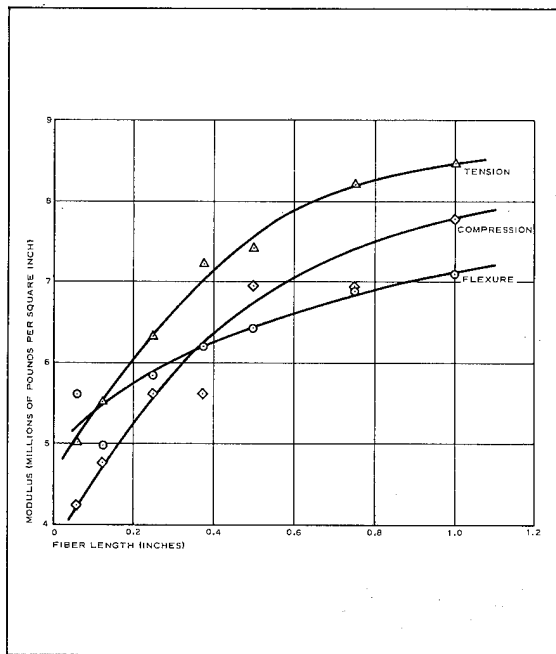


FIGURE 4: Modulus Properties of Noncontinuous Glass-Reinforced Epoxy Molding Compound

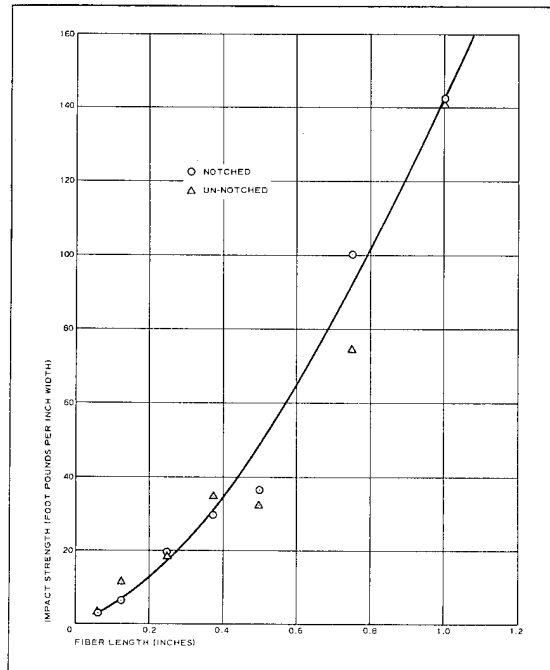


FIGURE 5: Impact Strength and Notch Sensitivity

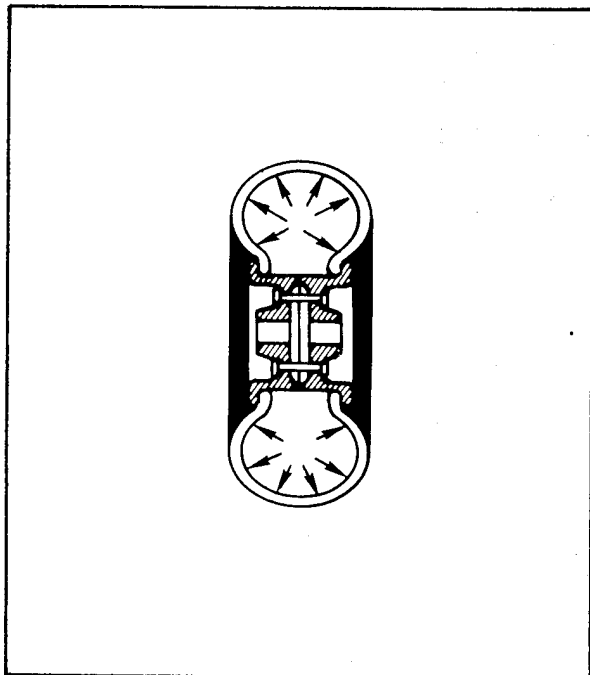


FIGURE 6: Burst Test

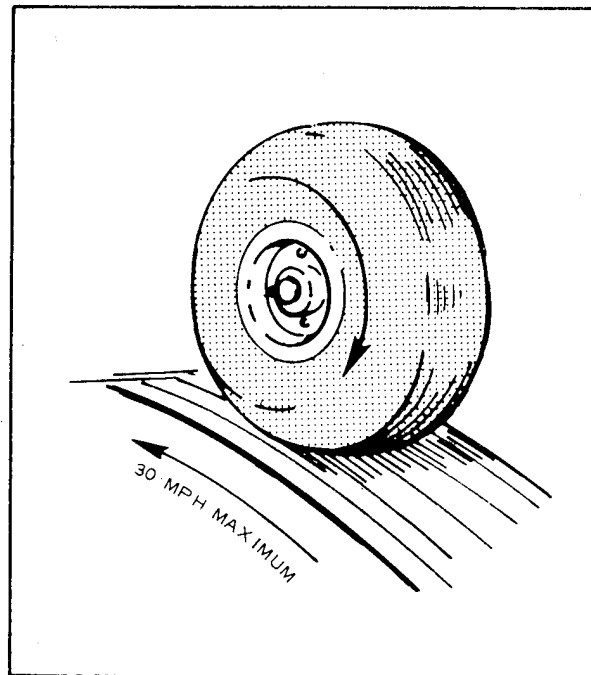


FIGURE 7: Roll Test

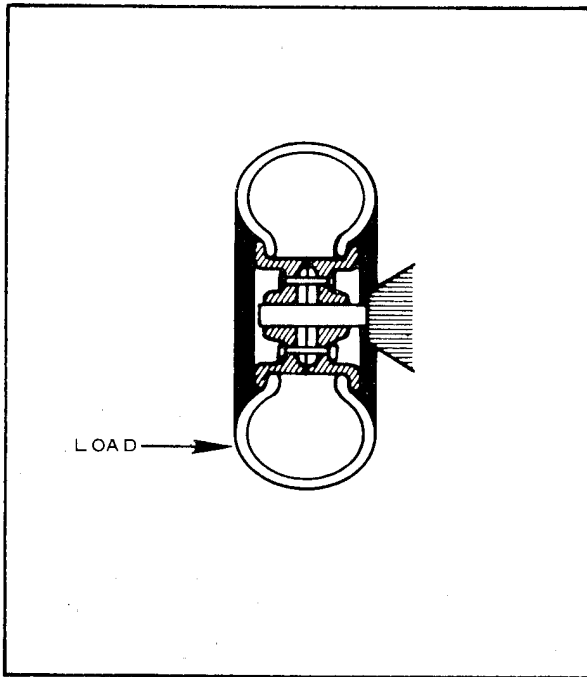


FIGURE 8: Axial Test

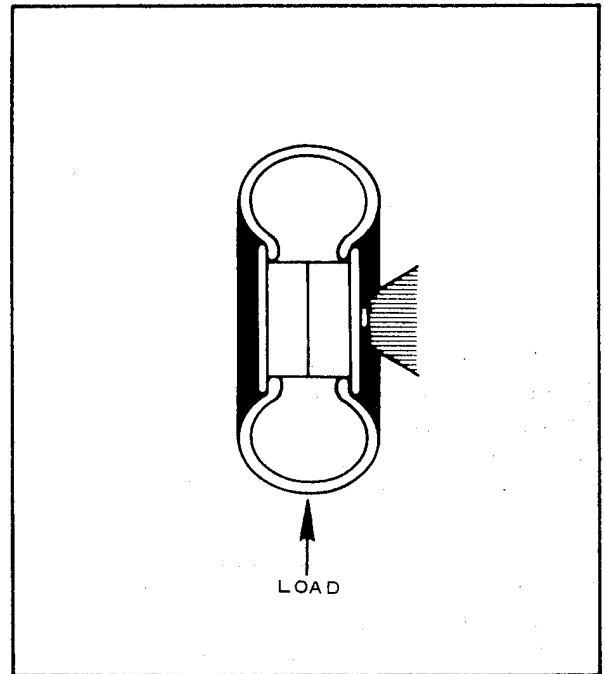


FIGURE 9: Radial Test



FIGURE 10: Plastic Helicopter Wheel (6.50 - 10), Inboard Half

8970-7
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SURLYN, A NEW POLYMER

E. I. du Pont de Nemours & Co.

Detroit, Mich.

In September 1964 Du Pont announced a new family of thermoplastic materials called "Surlyn" ionomer resins. Prior to that time, some market development work had been done with its precursor, Polymer A. In April 1965 we announced a commercial plant for the production of "Surlyn" A and established a price list for a series of "Surlyn" A resins.

Because of the unique polymer structure of this new material, we coined the generic term ionomer to indicate that this was a polymer with ionic bonds in addition to the normal covalent bonds. These ionic bonds are made possible by creating active sites on the polymer chain by introducing acid groups and then linking these active sites together with metallic ions. "Surlyn" A is a copolymer of methacrylic acid and ethylene to which has been added metallic ions such as sodium, potassium, magnesium and zinc.

It's easy to see that the ionomers can be tailored to a wide variety of end uses. The ionic forces modify crystalline structure in such a way that most of the ionomers are completely transparent resins. The ionic bonding also improves the following properties - strength, toughness, resilience, adhesion, oil resistance and melt strength. When comparing the stress-strain curves for one of the ionomer resins with a .920 density polyethylene and an EVA copolymer, you will note that the initial yield point is significantly higher for the ionomer. The ultimate tensile strength is nearly three times greater for the ionomer than for the low density polyethylene. If the resistance to oil penetration of an ionomer resin is compared to a high density polyethylene and medium density polyethylene, at 125°F, it takes about 1½ times longer for oil to penetrate a 1 mil thick film of ionomer than high density polyethylene.

Since the outstanding properties of "Surlyn" A ionomer resins is a combination of clarity and toughness, we'd like to compare "Surlyn" A with acetate, PVC and low density polyethylene. Tensile strength of the ionomers is significantly greater than the other three materials. Izod impact strength of "Surlyn" compares favorably with high density. Unnotched impact is exceptionally good for ionomers even at extremely low temperatures. The heat distortion temperature for the ionomers is a little on the low side - about 100°F - which compares favorably with the other three materials. The brittleness temperature is exceptionally low at less than 160°F below zero. Dielectric properties are comparable to polyethylene.

When the toughness of "Surlyn" A is compared to other transparent thermoplastics, you'll note that it's almost four times tougher than the cellulose.

With the exception of polystyrene, "Surlyn" A is the lowest price on a cents/cubic inch basis, compared to polycarbonate, cellulose and acrylics. We can process the ionomers in essentially the same way that we process polyethylenes. In comparing snake flow vs. melt temperature, the slope of the curve for the ionomers

is significantly steeper than that for low density polyethylene. This means that a change of cylinder temperature for example, from 400 to 450 will give us a very significant change in flow as compared with polyethylene.

In injection molding, we've learned that "Surlyn" has a great affinity for highly polished metals, and, consequently, we've had to develop a molding resin containing a mold release. We've found it extremely difficult, if not impossible, to use pinpoint gating. However, with gating designed for butyrate, acetate or acrylics, we've been able to fill the cavities with no difficulty. We've found it advantageous to use extremely cold molds using refrigerated water, if possible, as a coolant. In some cases, with extremely heavy sections, we've found it advantageous to take the part out of the mold as soon as the skin is set and then let it continue to cool in cold water. "Surlyn" A does not have high shrinkage and, consequently, there is little tendency to pull voids or sink marks.

Among applications for "Surlyn" A is a skin packaged item where "Surlyn" A was found to give good adhesion to the board and the transparency improved the appearance of the product. A pin cushion may be skin packaged to a board with "Surlyn" A film. This does not represent a commercial application but will give you an idea of the toughness of the melt since the pins have not penetrated the "Surlyn" A film.

In a "Polycard" where the film is formed and then packaged around the product (in this case a light bulb), it seems to suspend it in mid-air. "Surlyn" A appears to be quite promising for this application.

We have three commercial applications for extruded shapes - one is tubing which is used as a level indicator for 55 gallon drums. The chemical resistance of "Surlyn" A makes this a good application since "Surlyn" A can handle a variety of liquids without any corrosion problems. A second is a "step-on", an extruded shape which is used over carpeting or wooden steps to reduce the wear on the carpet or the step. In a third, our Freon Department is using "Surlyn" A covers on their drums and cans of solvents to keep the dirt out of them while they are in storage.

One of the first commercial applications for "Surlyn" A in molding was the little windows on the IBM typewriters. Here toughness, abrasion resistance and chemical resistance were the reasons why IBM picked "Surlyn" A. In Europe, women's shoe lifts out of "Surlyn" A are commercial and found to be quite attractive from a cost standpoint. They have about the same degree of abrasion resistance as nylon and will outwear the urethanes and rubber. A company in Canada is using injection molded putty knife handles from "Surlyn" A because of the resistance to the solvents that are normally encountered by painters. Screwdriver handles offer a good potential for "Surlyn" A because of its clarity.

A candy dish or boat molded in Japan out of "Surlyn" A gives the appearance of crystal.

A cover for an electric drill is injection molded in Europe. The drill is placed on a box and the cover is used as the top.

A company on the West Coast has developed a new maul handle in which they used a fiberglass reinforced handle and then use an insert in the mold to mold a "Surlyn" A handle or grip over the fiberglass. Cigar tips molded out of "Surlyn" A appear to be a commercial reality at this time. Another possibility for "Surlyn" A is steering wheels. In this case, we've had to develop a special ultraviolet resistant material which is now being tested by the automotive companies.

"Surlyn" A is a new material with unusual ionic bonds which give it a

combination of clarity, toughness and processability not found in other materials. It is a medium priced resin and is rapidly finding its place in the plastics industry for films, coatings, extruded shapes and molded items.

**INITIATION FEE
MUST BE ATTACHED
FOR PROCESSING.**



SOCIETY OF PLASTICS ENGINEERS, INC.
65 Prospect Street, Stamford, Conn. 06902
348-7528 AREA CODE 203

MEMBERSHIP APPLICATION
PLEASE PRINT OR TYPE

Executive Office Use Only

I.D. No. _____
Ack. _____
Elected _____

I hereby make application for ☐ admission into ☐ reclassification within ☐ reinstatement in } the Society of Plastics Engineers, Inc. in the grade of membership indicated below for which I believe I am qualified.
(See instructions on reverse side.)

Grade	Initiation Fees	Annual Dues	Foreign Dues	I wish to affiliate with the _____
<input type="checkbox"/> Senior Member	\$10.00	\$20.00	\$17.50	_____
<input type="checkbox"/> Member	10.00	20.00	17.50	_____
<input type="checkbox"/> Affiliate Member	10.00	20.00	17.50	_____
<input type="checkbox"/> Student Member	None	5.00	5.00	_____ section.

(Geographical location. See listing on reverse side.)

Applicants Full Name _____
(First) (M.I.) (Last) (Citizen of) (Birthdate)

Please fill in both addresses and **CHECK THE ONE TO WHICH YOUR MAIL SHOULD BE ADDRESSED.**

☐ **BUSINESS:** Company Name and Division: _____
Position _____
Address _____ City _____ State _____ Zip Code _____
☐ **HOME:** Address _____ City _____ State _____ Zip Code _____

REFERENCES The By-Laws require the names of three references who are familiar with your work. One of them should be a member of the Society. Assistance in providing member-references, when needed, will be given on request.

1. _____ Address _____
2. _____ Address _____
3. _____ Address _____

STATEMENT OF COLLEGE WORK

Years Attended		Institution	Major and Minor	Degree	Experience Credits See reverse side
From	To				
Total Education Experience Credits					

RECORD OF QUALIFYING EXPERIENCE IN PLASTICS

Dates				Give your title, name and location of employer, and name of immediate superior for each position. List in chronological order. Describe duties fully and state briefly any important engineering work you have done in each position. If space is not sufficient, use a separate sheet.	Time in years and months
From	To	Mo.	Yr.		

I certify that the statements made in this application are correct. I agree, if elected, to be governed by the Constitution and By-Laws of the Society, and to promote the objective of the Society.

Total qualifying years of experience.

Total education and qualifying experience credits.

CREDENTIALS COMMITTEE USE ONLY

Approved (Signature) _____ Date _____

Approved (Signature) _____ Date _____

Date of Application _____

Signature in ink. _____

COMPLETING THE APPLICATION

Grade of Membership . . .

Membership grades are based on experience credits which are earned as follows:

1. Experience credits earned for education.

- Doctorate in science or engineering subject: **6 credits**
- Masters in science or engineering subject: **5 credits**
- Bachelors in science or engineering subject: **4 credits**
- Other degree in non-science or non-engineering subject: **2 credits**

Maximum credits allowable for education shall be six (6).

When filling in the "Statement of College Work" on the reverse side of this application, please place the corresponding number of credits earned in the right-hand column.

2. Experience credits for qualifying experience in plastics or plastics engineering are earned at the rate of one (1) per year, e.g. 5½ years of qualifying experience = 5½ credits. Please detail carefully the engineering skill required for each position to help the Credentials Committee judge experience as "qualifying."

When filling in the "Record of Qualifying Experience in Plastics" on the reverse side, please place the amount of time spent in each position (in years and months) in the right-hand column.

When you have determined the number of credits which you believe you have earned consult the following membership grade requirements. Indicate on the reverse side the grade of membership for which you believe you are qualified.

GRADE	REQUIREMENTS
Senior Member	Minimum of twelve (12) experience credits and maintained continuous membership in the Society for a minimum of two (2) years.
Member	Minimum of six (6) experience credits
Affiliate Member	Less than six (6) experience credits
Student Member	Regularly enrolled student (full- or part-time) in a course of study in plastics and between the ages of 16 years and 26 years, inclusive.

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DETROIT	ROCKY MOUNTAIN
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EASTERN NEW ENGLAND	SOUTH TEXAS
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MID-MICHIGAN	TRI STATE
MILWAUKEE	UPPER MIDWEST
MONTERREY	VIRGINIA-CAROLINA
NEW YORK	WESTERN MICHIGAN
NEWARK	WESTERN NEW ENGLAND
NORTH TEXAS	NON-SECTION



MEMBERSHIP APPLICATION

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65 Prospect Street, Stamford, Conn. 06902

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